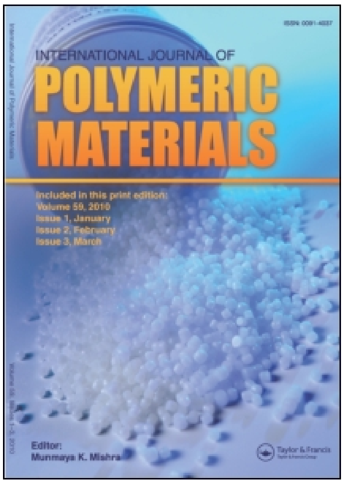

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Preparation and Use of Nano Zinc Oxide in Neoprene Rubber

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Zinc oxide (ZnO) of nanometer particle size was prepared by solid-state pyrolytic method. TEM, XRD, and surface area studies showed that the prepared zinc oxide had particle size in the range of 15–30 nm and surface area in the range of 12–30 m^2/g. This nano zinc oxide was used as a curing agent in neoprene rubber. The optimum dosage of ZnO was found to be low compared to commercial ZnO. The cure characteristic and mechanical properties were compared with those containing conventional ZnO. It was found that a low dosage of zinc oxide was enough to give equivalent curing and mechanical properties compared to one containing a higher dosage (5 phr) of commercial zinc oxide in neoprene rubber.

Keywords: nano zinc oxide, neoprene rubber, solid-state pyrolytic method

INTRODUCTION

Nanotechnology and the development of nanocrystalline materials is the challenge of this age. Several application areas being envisaged for these new classes of materials stimulated intensive investigations. Zinc oxide of nanometer range particle size has been paid much attention for its unique properties. It is widely used for solar energy conversion, nonlinear optics, catalysis, varistors, pigments, gas sensors, and cosmetics [1–10]. Zinc oxide (ZnO) is added to natural rubber compounds as an activator to activate sulfur vulcanization and thereby reduce the vulcanization time, whereas in neoprene rubber it is used

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as curing agent. Besides its effect on the curing process, ZnO has many beneficial effects on the physical properties of rubber [11]. Furthermore, ZnO assists in the processing of uncured rubber [12]. For the protection of the environment and because of upcoming legislation regarding the use and application of ZnO and zinc-containing compounds, it is considered desirable to study the possibilities of reducing the ZnO content in rubber products.

ZnO is a dense material that tends to compact and disperse with difficulty. Therefore, it is distributed in the form of crystal particles in rubber mixes [13]. Nieuwenhuizen in his thesis proposed a mechanism in which the ZnO surface functions both as a reactant and as a catalytic reaction template, activating and bringing together reactants [14]. Molecules of accelerators, sulphur, and fatty acids diffuse through the rubber matrix and are adsorbed onto ZnO with the formation of intermediate complexes. An important parameter in this mechanism is a uniform dispersion of inorganic ZnO throughout the organic polymer matrix. The efficiency of ZnO during vulcanization can be enhanced by the maximization of the contact between the ZnO particles and the accelerators in the compound. This contact is dependent on the size of the particles, their shape, and their specific surface area. In some rubbers, such as natural rubber (NR) and ethylene-propylene-diene rubber (EPDM), there is evidence that a considerable amount of ZnO is consumed and transformed into ZnS [15–17]. The zinc content in rubber products has come under increased scrutiny due to environmental concerns. The trend in the industry is, therefore, to reduce the zinc content in rubber products. In this study we prepared nano zinc oxide by solid-state pyrolytic method [18] and used it as curing agent in neoprene rubber.

EXPERIMENTAL

Materials

Zinc acetate and sodium bicarbonate were supplied by S.D. Fine-Chem. Ltd., Mumbai, India.

Solid-State Pyrolytic Reaction

2.2 g (10 mmol) of $Zn(CH_3COO)_2 \cdot 2H_2O$ and 2 g (23.8 mmol) of $NaHCO_3$ are mixed at room temperature. The mixture is pyrolyzed at 300°C for 3 h. The $Zn(CH_3COO)_2 \cdot 2H_2O$ is changed into ZnO nanoparticles, while the $NaHCO_3$ is changed into CH_3COONa and eventually washed away with deionized water. Consequently, white ZnO nanoparticles are obtained through the thermal decomposition process. Hereafter this zinc oxide will be called ZnO (P) and commercial zinc oxide as ZnO (C).

CHARACTERIZATION OF ZnO

The morphology and particle size of zinc oxide were observed using transmission electron microscopy (TEM). The transmission electron microscopy (TEM) image was taken on a JEOL GEM 3010 transmission electron microscope operating at 300 KV. X-ray powder diffraction (XRD) was used to characterize the zinc oxide powders. A Bruker, D8 advance Rotaflex diffraction meter using CuK$_\alpha$ radiation and $\lambda = 1.5406\,\text{Å}$ was used. The surface areas of the zinc oxide nanoparticles and commercial zinc oxide were measured using BET method. Surface area analysis was done by Micromeritics BJH surface analyzer Tri-Star 3000. Measurements were carried out under nitrogen adsorption at liquid nitrogen temperature. Infrared absorption spectra were collected using ThermoAvtar 370 spectrometer. Bulk density of ZnO (P) and commercial zinc oxide were measured as per ASTM D 1895.

RUBBER COMPOUNDING

Materials

Neoprene was manufactured by M/s DuPont USA with Mooney viscosity ML $(1+4)$ at 100°C of 47. NICE Chemicals Pvt. Ltd. supplied light magnesium oxide with specific gravity $2.62 + 0.2$. Stearic acid was supplied by Godrej Soap (Pvt) Limited, Bombay, with melting point of 65°C and acid number 200. High abrasion furnace black (N 330) [HAF] was supplied by M/s Philips Carbon Limited, Kerala, India, with DBP absorption 102 ± 5CC/100 g and iodine number 82. Dioctyl phthalate (DOP) was commercial grade and was supplied by Rubo Synthetic Impex Ltd., Bombay, with specific gravity 0.986 g/cm^3. Antioxidant HS (1,2 dihydro–2,2,4-trimethyl quinoline polymerized) was obtained from Bayer India Limited, having specific gravity of 1.1 g/cm^3. Commercial zinc oxide was supplied by M/s Meta Zinc, Bombay, with specific gravity 5.5 g/cm^3.

Table 1 shows the formulation of various mixes. In order to optimize the amount of ZnO (P) for curing in neoprene compounds, the concentration of ZnO prepared from solid-state pyrolytic method was changed from 1 to 2 phr as shown in Table 1.

TABLE 1 Formulation Used for Neoprene Rubber

Compounding ingredients (phr)	Mix I	Mix II	Mix III
Neoprene W	100	100	100
Light MgO	4.0	4.0	4.0
Stearic acid	1.0	1.0	1.0
HS	1.0	1.0	1.0
HAF	40	40	40
DOP	8.0	8.0	8.0
ZnO	5.0 (C)	1.0 (P)	2.0 (P)
Na22	0.5	0.5	0.5

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, homogenization of the compound was carried out by passing six times through tight nip gap and finally sheeted out.

Cure characteristics of the mixes were determined at 150°C using Rubber Processing Analyzer RPA 2000 Alpha technologies, USA, as per ASTM D2084-01. Vulcanization up to optimum cure time was then carried out in an electrically heated hydraulic press kept at 150°C. The moldings were cooled quickly in water at the end of the curing cycle and stored in a cool dark place for 24 h.

Mechanical Properties

The vulcanizates were tested for mechanical properties according to relevant ASTM standards. The tensile properties were measured using Shimadzu Universal Testing Machine model AG-1 50 KN according to ASTM D 412. Samples were punched out from the molded sheet using a dumb-bell-shaped die. The crosshead speed was maintained at 500 mm/min. The tear strength was determined according to ASTM D-624 using angular specimens punched out from the molded sheet. The test speed was 500 mm/min. The hardness of the sample (Shore A) was determined using Zwick 3114 hardness tester according to ASTM D-2240. Compression set (%) was determined according to ASTM D 395-86 (Method B). The compression set was calculated using the following expression

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

where

t_0 = initial thickness of the specimen
t_1 = final thickness of the specimen
t_s = the thickness of the spacer bar.

The abrasion resistances of the samples were tested using DIN 53516. Cylindrical samples of 15 mm diameter and 20 mm length were kept on a rotating sample holder and 10 N loads were applied. Initially a pre-run was given to the samples and their weight was taken. Each sample was then given a complete run and the final weight was noted. The difference in weight is reported as the abrasion loss. It is expressed as the volume of the test-piece getting abraded by its travel through 42 m on a standard abradant surface. The abrasion loss was calculated as follows:

$$V = \frac{\mathrm{m}}{\rho}$$

where

V = abrasion loss
m = mass loss
ρ = density of the sample

The heat build-up was measured using the Goodrich flexometer conforming to ASTM D 623-78 (Method A). Cylindrical samples of 25 mm height and 19 mm diameter were used to carry out the test. The oven temperature was kept constant at 100°C. Each sample was preconditioned to the oven temperature for 20 min. The heat development at the base of the sample was sensed by a thermocouple and relayed to a digital temperature indicator. The temperature rise (ΔT°C) at the end of 20 min was taken as the heat build-up. De Mattia flex resistance of the vulcanizates was determined using a Wallace De Mattia flexing machine as per ASTM D 430-57 T.

Swelling Studies

The swelling index (in %) of the vulcanizates was evaluated as follows. Samples of 10 mm diameter and 2 mm thickness were punched out from the central portion of the vulcanizates, weighed as initial weight (W_1) and then allowed to swell in different solvents for 3 d. Samples were weighed again as swollen weight (W_2).

$$\text{Swelling index} = \frac{W_2 - W_1}{W_1} \times 100$$

Crosslink Density

The chemical crosslink density of the vulcanizates was evaluated as follows. Samples of approximately 10 mm diameter and 2 mm thickness and 0.2 g weight were punched out from the central portion of the vulcanizates and allowed to swell in methyl ethyl ketone for 24 h then the samples were weighed again. The volume fraction of rubber, V_r, in the swollen network was then calculated by the following equation [19]:

$$V_r = \frac{(\mathrm{D\text{-}FT})\rho_{\mathrm{r}}^{-1}}{(\mathrm{D\text{-}FT})\rho_{\mathrm{r}}^{-1} + \mathrm{A}_0\rho_{\mathrm{s}}^{-1}}$$

where

T = weight of the test specimen
D = weight of the deswollen test specimen
F = weight fraction of insoluble components
A_0 = weight of the absorbed solvent corrected for the swelling increment
ρ_{r} = density of the rubber
ρ_{s} = density of the solvent

The volume fraction V_r is calculated assuming that the filler does not swell. It is then converted to V_{r0} (the value V_r would have in the absence of filler) according to Cunneen and Russel [20]

$$\frac{V_{r0}}{V_r} = ae^{-z} + b$$

Here "a" and "b" are constants characteristic of the system and "z" is the weight fraction of the filler in the vulcanizate. The total chemical crosslink density was calculated using the Flory-Rehner equation [21,22].

$$\text{Crosslink density} = \frac{-[\ln(1 - V_{r0}) + V_{r0} + \chi V_{r0}^2]}{2\rho_r V_s (V_{r0})^{1/3}}$$

V_s = molar volume of the solvent
χ = a parameter characteristic of the interaction between rubber and solvent.

Aging Studies

Aging tests were carried out for 24, 48, 72 and 96 h in accordance with ASTM 573-88 using an air oven at 100°C. Tensile properties and tear resistance of the samples were determined for specified periods.

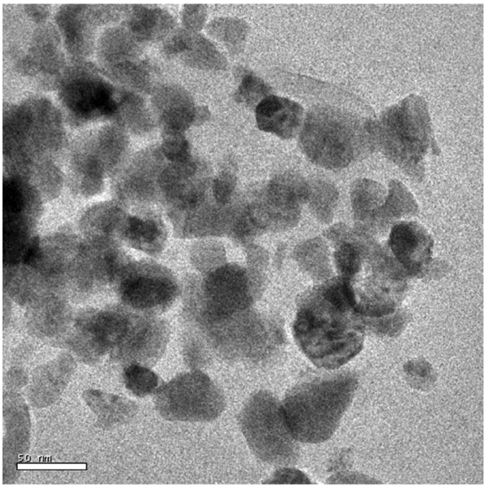
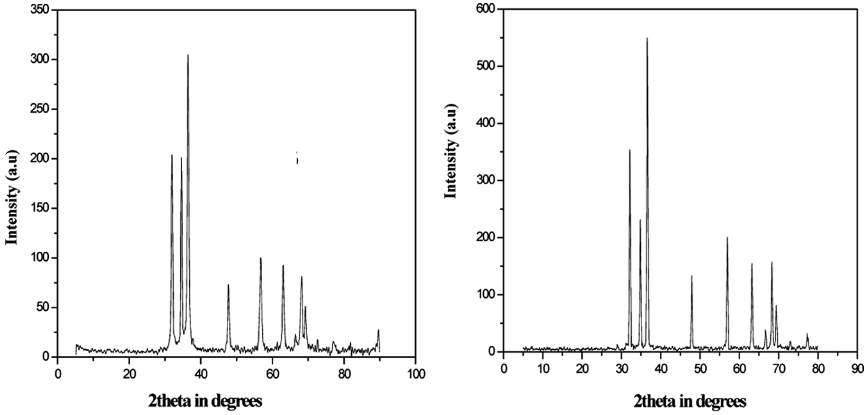


FIGURE 1 TEM image of ZnO (P) nanoparticles.

RESULTS AND DISCUSSION

ZnO Characterization

Figure 1 shows a TEM image of zinc oxide prepared by solid-state pyrolytic method. It shows that the particles of ZnO (P) have an average size of 30 nm.



(a) (b)

FIGURE 2 XRD patterns of (a) ZnO (P) and (b) ZnO (C).

TABLE 2 Surface Area and Bulk Density of Zinc Oxide Samples

SI. No.	Samples	Surface area	Bulk density
1	ZnO (C)	4.35 sqm/g	0.6 g/cm^3
2	ZnO (P)	12.13 sqm/g	0.4 g/cm^3

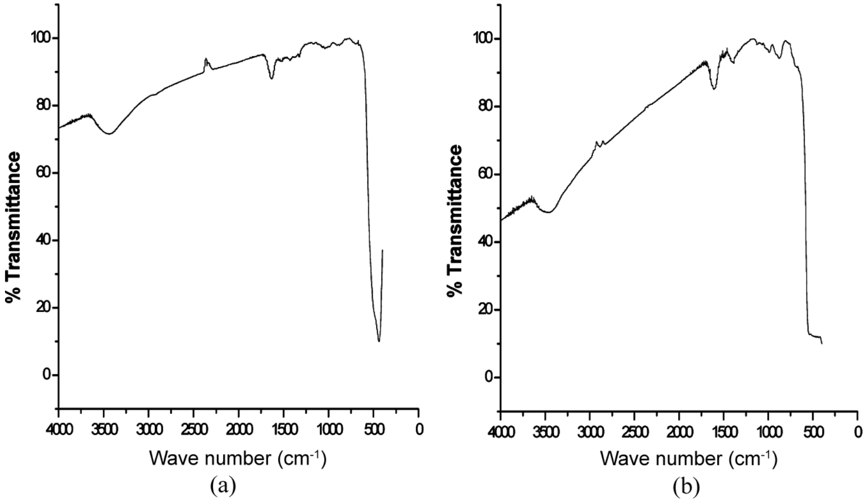
Figure 2 shows the XRD patterns of ZnO samples. The average particle size for zinc oxide prepared by solid-state pyrolytic method ranges from 15–25 nm and the average particle size of commercial zinc oxide range from 45 nm to 60 nm.

Table 2 shows the surface area and bulk density for ZnO (C) and ZnO (P) samples. The surface area is found to be 3 times higher for ZnO (P) than that of ZnO (C). Bulk density is also found to be low for ZnO (P) compared to ZnO (C).

Figure 3 shows the IR spectra of ZnO samples. The peak around 450 cm^{-1} shows a distinct stretching mode of zinc oxide.

Cure Characteristics

Table 3 shows the cure characteristics of various mixes and Figure 4 shows the cure curves of the compounds with varying concentration of zinc oxide. It is seen that at 150°C, the curing of mix II with 1 phr ZnO (P) is slow compared to mix III containing 2 phr of ZnO (P).



(a)

(b)

FIGURE 3 FTIR spectrum of (a) ZnO (P) and (b) ZnO (C).

TABLE 3 Cure Characteristics of Mixes with Varying Concentration of Zinc Oxide

Mix	Mix I	Mix II	Mix III
Optimum cure time T_{90}	19.27	22.12	19.6
Scorch time T_{10}	1.70	1.70	1.73

Comparing the cure characteristics of mix I and III, mix I with ZnO (C) (5 phr) and mix III with Zno (P) show almost the same scorch time and cure time.

Mechanical Properties

Table 4 shows the comparative evaluation of tensile properties of mix I, II and III. Upon comparison, mix III with 2 phr ZnO (P) had better tensile properties than mix II with 1 phr ZnO (P). This shows that the dosage of ZnO (P) as curing agent is optimized at 2 phr ZnO (P). Comparing the properties of mix I and mix III, mix III with 2 phr of ZnO (P) had better tensile properties than mix I with 5 phr of ZnO (C). Table 5 shows the other mechanical properties of mix I and III. It is seen that the mechanical properties of mix III are better

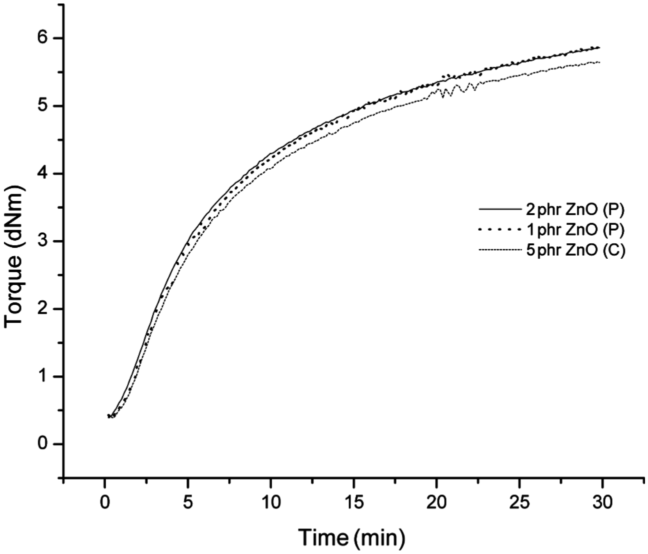


FIGURE 4 Cure curves of the compounds.

TABLE 4 Tensile Properties of Neoprene Rubber Vulcanizates

Mix	Tensile strength (N/mm^2)	300% modulus (MPa)	Elongation at break (%)	Tear strength (N/mm)
Mix I	19.82	8.47	489	52.98
Mix II	13.08	8.27	480	52
Mix III	18.38	8.9	468	59.65

TABLE 5 Mechanical Properties of Neoprene Rubber Vulcanizates

Mix	Hardness (Shore A)	Compression set (%)	Abrasion loss (cc/hr)	Crosslink density ($g/mol/cm^3$)	Heat build up (ΔT)°C	Flex resistance (k cycles)
Mix I	67	19.1	2.625	7.38×10^{-5}	13.2	30971
Mix III	67	18.43	2.411	7.94×10^{-5}	13.3	62830

than those of mix I. This may be due to the crosslinking in mix III being higher than mix I.

Swelling Studies

Table 6 shows the swelling studies of mix I and mix III in solvents like toluene, cyclohexane, petrol, diesel and engine oil. The swelling index value for mix III is low compared to mix I. This may be due to the higher crosslinking in mix III.

Aging Studies

Table 7 shows the mechanical properties of neoprene vulcanizates after aging at 100°C for 96 h. The retention in properties is comparable for both vulcanizates (mix I and mix III).

TABLE 6 Swelling Indexes of Mix I and Mix III in Various Solvents

Solvent	Mix I (%)	Mix III (%)
Toluene	126	122
Cyclohexane	43	41
Petrol	26	25
Diesel	24	23
Engine oil	41	38

TABLE 7 Mechanical Properties After Aging at 100°C for 24, 48, 72 and 96 h

	Mix I				Mix III			
Hours	Tensile strength (MPa)	300% modulus (MPa)	Elongation at break (%)	Tear strength (N/mm)	Tensile strength (MPa)	300% modulus (MPa)	Elongation at break (%)	Tear strength (N/mm)
24	16.37	10.50	399	55.33	15.30	11.05	369	52.64
48	17.12	12.20	383	45.92	15.85	11.71	373	50.17
72	16.59	12.32	366	47.92	15.59	12.40	351	51.15
96	16.58	12.59	366	39.85	14.09	12.86	322	51.61

CONCLUSIONS

Zinc oxide with particle size in nanorange could be prepared by solid-state pyrolytic method. The compounds containing a lower dosage (2 phr) of the zinc oxide prepared by this method were found to have equivalent cure rate and better mechanical properties than compounds with 5 phr commercial zinc oxide. Swelling studies show higher crosslinking for vulcanizates containing a low amount of ZnO (P). The aging resistance was found to be comparable.

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