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Synthesis And Application of Nano Zinc Oxide in Fabrication of Rubber Composites

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Abstract

Nano zinc oxide (ZnO) has garnered significant attention in recent years due to its unique properties and potential applications in various fields. This paper discusses the synthesis of nano ZnO by precipitation method and characterizes them with various techniques such as X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), and Fourier Transform Infra-Red (FTIR) Spectroscopy and explores its application in the preparation of rubber composites. These synthesized particles were measured to have an average size of 29.78 nm using X-ray diffraction. SEM/EDS findings provide significant new insights into the morphological and elemental properties of the synthesized ZnO nanoparticles.FTIR is used to analyze the chemical and structural properties of ZnO nanoparticles. The integration of artificial nanoparticles into the rubber matrix through the use of two roll mills is the additional focus of this work. Using nano ZnO at varying loading concentrations (0.5 to 6 phr), the effects of nano additives were evaluated in rubber compounding. The paper highlights the impact of nano ZnO on the physical, cure properties of rubber composites, emphasizing its role in enhancing tensile properties at 1phr of synthesized nano ZnO with rubber composite. The paper discusses the challenges of integrating nano ZnO into rubber matrices and offers insights into future research directions.

Keywords: Zinc oxide, nanoparticles, tensile properties, cure properties, rubber composite

INTRODUCTION

Rubbers are those polymers that are more precisely known as elastomers. Elasticity i.e. instantaneous and complete recovery after removal of the load is the most versatile property of rubbers. Products which are made out of this polymer are inevitable these days due to wide range of applications. Vulcanization is one of the most significant methods to enhance the workability of rubber compounds. It enhances elasticity as well as durability under severe conditions. Crosslinking between rubber particles plays a vital role in making the polymer to be more elastic and durable [1][2]. Several popular ways of crosslinking include peroxide crosslinking [3][4]. irradiation crosslinking [5]. and sulfur crosslinking [6]. etc. The most common and widely used is sulfur vulcanization but it takes place at a very high temperature and needs a long time to accomplish. To facilitate this process, some additional additives such as accelerators, activator (ZnO), oils, antioxidants, etc. have also been added to promote rubber vulcanization. Zinc oxide (ZnO) is one of the commonly used metal oxides, which is used for rubber vulcanization as an activator. The rate of

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cross-linking is enhanced using ZnO, due to the possible formation of zinc chelates with accelerates. Zinc polysulfide complexes are the outcome of such linkages which culminate into a crosslinked structure with rubber moieties. Several other positive benefits of ZnO are its antioxidant properties, antibacterial activities, and its role as a filler in rubber composites [3-8]. Rubber-based composites perform differently depending on filler particle size, shape, surface area, and surface reactivity in addition to filler dispersion and filler-rubber interaction. It has been noted that adding fillers, like carbon nanotubes and nano-ZnO, improves the thermal conductivity of rubber composites [7].Among all industries, the tire industry is considered as largest consumer of ZnO, which consumes almost 50% of total ZnO [8]. Several ill effects of ZnO on environment has taken the research orientation towards reduction in amount of ZnO in rubber compounding which can be done by using nano ZnO in place of conventional one.

In context to this we aimed to prepare nanoparticles of ZnO and utilize them in rubber composites to see their effect on various properties. Detailed study on synthesis and characterization of nano particles of zinc oxide is discussed herewith in the research paper Along with this, cure characteristics and mechanical characteristics of rubber composite are also detailed.

EXPERIMENTAL PART

Materials

Zinc acetate dihydrate [$Zn(CH_3COO)_2$ $2H_2O$] [molecular weight (M.W.) 293.6 g/mol], Sodium hydroxide, [MW. 39.99 g/mol], Stearic acid (M.W. 284.48), MBTS [Benzothiazyl Disulfide] (MW. 167.24 g/mol), Antioxidant 4020 [N-(1,3-dimethyl butyl)-N0-phenyl-p-phenylenediamin (6PPD)], sulfur powder (M.W. 32.06), Carbon black [molar mass- 12g/mol], Aromatic oil, Standard rubber grade zinc oxide (ZnO), Styene butadiene rubber was supplied by Reliance Industries Ltd., India.

METHODS

Nanoparticle Synthesis

ZnO nanoparticles were prepared using a precipitation method. ZnO nanoparticles were made by gradually adding 100 ml of 0.2 M NaOH to 100 ml of 0.1 M zinc acetate solution while stirring continuously. The resultant mixture was continuously stirred for three hours while it was kept at room temperature. The resulting white precipitate was centrifuged, repeatedly cleaned with distilled water, followed by ethanol, and dried in an oven for three hours at 100°C. Zinc (OH) 2 is transformed into zinc oxide during the drying process [9]. The preparation of ZnO nanoparticles schematic diagram is shown in Figure.1. The method was environmentally friendly.

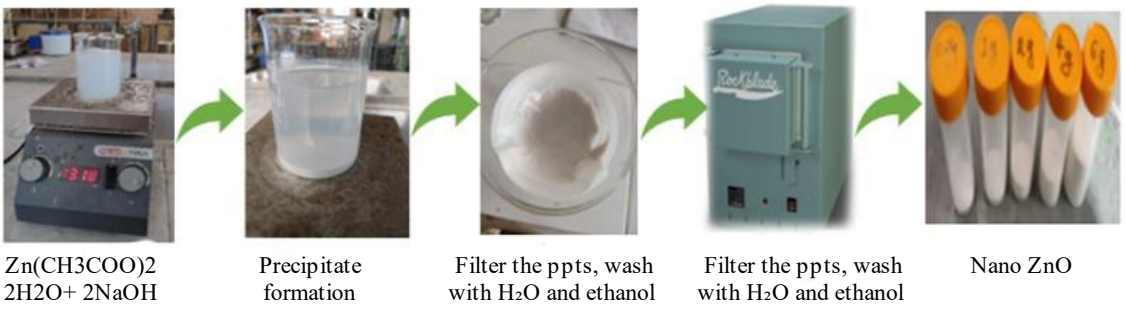

Figure 1. Diagram of preparation of zinc oxide nanoparticles.

CHARACTERIZATION TECHNIQUES OF SYNTHESIZED ZNO NANOPARTICLES X-RAY DIFFRACTION (XRD)

The size of the zinc oxide powder particles was determined using an X-ray diffractometer with a Cu_K-beta_1D generator (45 kV, 30 mA, with k = 0.15418 nm) and a Std Goniometer. The scans were conducted over a 2θ range of 5–90° with a step width of 0.01° and a step time of 10.00 °/min.

Scanning Electron Microscopy (SEM)

Synthesized zinc oxide nanoparticles were examined using a JEOL JSM-IT500 scanning electron microscope (SEM) with energy-dispersive X-ray spectroscopy (EDS).

Fourier Transform Infra-Red (FTIR) Spectroscopy

The FTIR spectroscopy measurements were accomplished using FT-IR Spectrum 2 (Perkin Elmer). All the absorption spectra measurements were recorded using a continuous IR light in the wavenumber range of 4000–400 cm^{-1}.

Fabrication of Rubber Composites

Equipment used: Electronic balance with (± 0.001 gm) accuracy, Hand Moulding press machine, two-roll mill Oscillating Disc Rheometer (ODR), Tensile test machine, and Durometer (ShoreA) hardness Tester.

Compounding Process of Rubber Composite

Compound recipes are presented in Table1 nano ZnO / rubber composites. The mixing processes were carried out at the Halol manufacturer, Badri Narain Rubbers Pvt Ltd.

In a laboratory, the important additive materials, synthesized zinc oxide nanoparticles with different loadings (0.5-6)phr, and rubber are mixed using a two-roll mill. The mixing schedule, which can be found in Table 1, was followed when mixing. The distance between the two rolls was reduced to a maximum of (0.5–1) mm by repeatedly passing rubber between them. Rubber bits and other important additives were repeatedly passed between rollers at room temperature while adhering to the correct protocols to produce homogenous materials.

Table 1. Formulation and Compound Designation for nano ZnO/rubber Composites

Ingredients (phr)	**Quantities of samples**				
	Sample-1	***Sample-2***	***Sample-3***	***Sample-4***	***Sample-5***
Rubber	100	100	100	100	100
Stearic acid	2	2	2	2	2
Accelerator (MBTS*)	1.5	1.5	1.5	1.5	1.5
carbon black	20	20	20	20	20
Aromatic oil	6	6	6	6	6
Antioxidant 4020	0.5	0.5	0.5	0.5	0.5
Sulfur	2	2	2	2	2
Nano ZnO	0.5	1	2	4	6

**Mercatobenzothiazyl Disulfide*

CHARACTERISTICS OF FABRICATED RUBBER COMPOSITES

Cure Characteristics

Cure characteristics of the rubber compounds were tested by the Oscillating Disc Rheometer by following ASTM D 2084.Torques (M_H-M_L), scorch time (ts_2), and curing time (tc_{90}) were evaluated with an Oscillating Disc Rheometer. The temperature was kept at 150° C during testing of composites.

Tensile Properties

Tensile tests were conducted at 500 mm/min crosshead speed following ASTM D412 standards.

Tensile tests were performed using the tensile machine to determine tensile properties like elongation at break and tensile strength. Three samples were tested, and the results were averaged. They also computed their standard deviation. At room temperature, these tests were carried out. Wallace Test Sample The vulcanized sheets were cut with a cutting press to create the test sample or dumbbell test shape (33mm ×6mm×1.3 mm) of the dumbbell, a dial gauge was employed.

Hardness

The surface hardness of the fabricated samples was measured using a ShoreA Durometer under the following ASTM D 2240. All reported values were averages of 3 test results, with standard deviation calculated for each fabricated sample.

RESULTS AND DISCUSSION

Characteristics of Nano ZnO

X-ray diffraction (XRD)

The XRD pattern of the synthesized nano ZnO is shown in Figure 2. The diffraction peaks observed at 2θ values of approximately 29.56 °, 33.74 °, 36.47°, 47.74° 56.79°, and 63.07° correspond to the (100), (002), (101), (012), (110) and (013) crystallographic planes of hexagonal of ZnO, respectively. For nano, ZnO observed peaks corresponding to a hexagonal structure. The lattice parameters for ZnO are typically observed around a= 3.2533 Å c= 5.2073 Å. The average crystallite size was calculated to be 29.78±5nm for the synthesized ZnO nanoparticles. It should be noted that crystallite size is assumed to be the size of a coherently diffracting domain. It is not necessarily the same as particle size. The (100) peak is more intense than the (002) peak, but less so than the (101). This demonstrates that the orientation of ZnO nanoparticles in the specimen studied is predominantly along (100) [10].

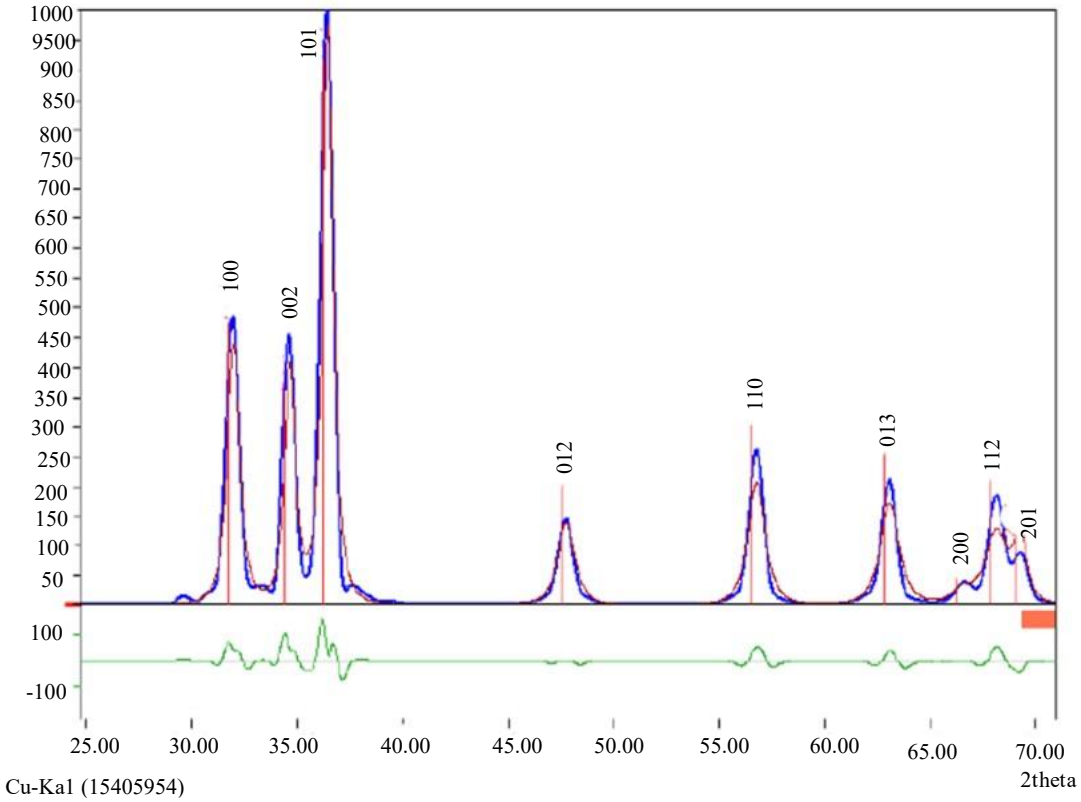

Figure2. XRD pattern of synthesized ZnO Nanoparticle.

Scanning Electron Microscopy (SEM)

According to SEM analysis, the calcined ZnO powder is made up of aggregates of ZnO particles. The particles are all identical and spherically shaped. The SEM images of ZnO NPs, are shown in Figure 3. This confirms that the particles are nano ZnO that have been synthesized. The SEM micrograph also shows homogeneous sizes and intricate structures.

It can be confirmed that the nanoparticles are made of ZnO by looking for peaks in the EDS spectrum Figure 4 that represent the elements zinc (Zn) and oxygen (O). If the EDS spectrum displays no peaks corresponding to any other element, the synthesized ZnO nanoparticles are deemed pure. These findings provide important new insights into the morphological and elemental properties of the generated nanoparticles[11]. The x-axis shows energy (keV), while the y-axis shows intensity (counts). The spectrum contains energy peaks for oxygen in the K-shell at 0.6 keV and zinc in the L-shell at 0.8, 1

and K-shell at 8.4, and 9.7 keV. SEM analysis confirms the synthesized nano ZnO's spherical morphology and uniform size distribution, while EDS analysis confirms its highly pure ZnO composition.

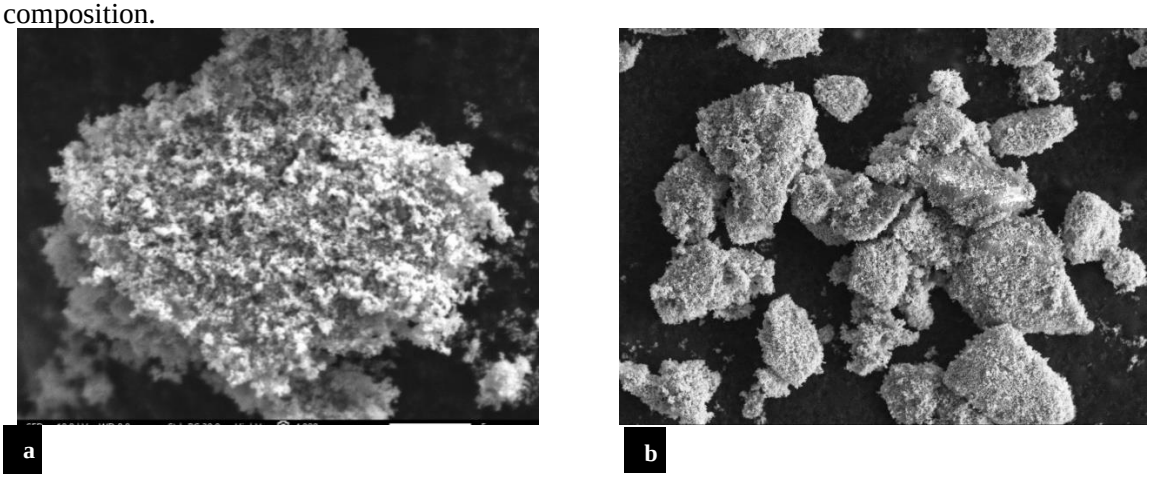

Figure 3. Scanning electron microscopy (SEM) images of synthesized ZnO NPs with different magnifications (a) 3000× magnification (b) 1000× magnification.

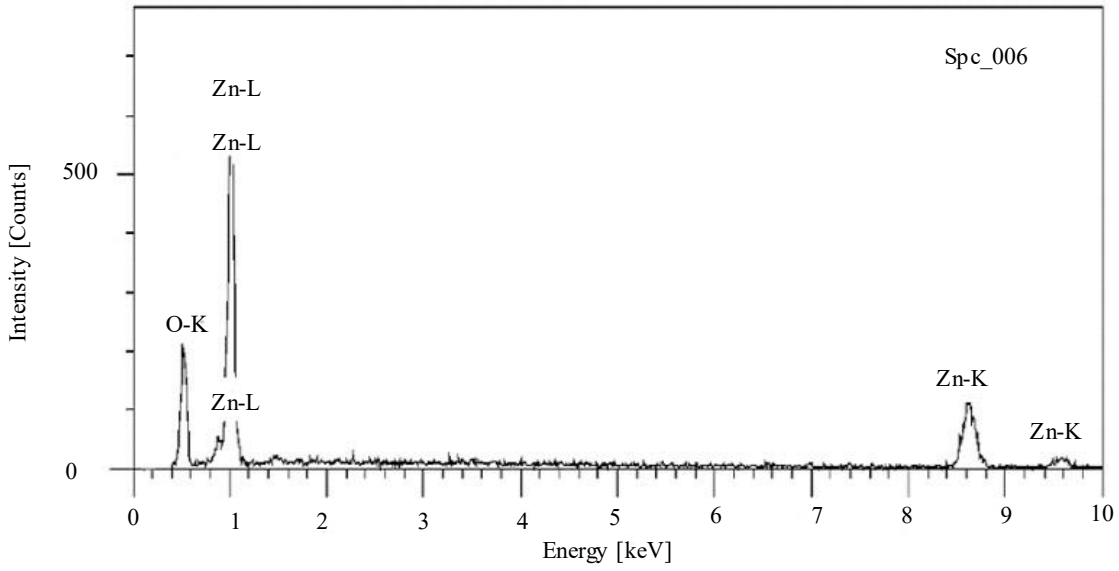

Figure 4. EDS spectra of synthesized ZnO nanoparticles.

Fourier-Transform Infrared Spectroscopy (FTIR)

Figure 5 shows that FTIR analysis of nano ZnO was performed using the KBr in the wave number range of 400 to 4000 cm-1.FTIR bands of preparared ZnO nanoparticles are listed in Table2.The FTIR analysis of nano ZnO revealed absorption peaks at 3399 cm^{-1}, 2925 cm^{-1}, 1625 cm^{-1}, 1454 cm^{-1}, 1383 cm^{-1}, 1103 cm^{-1}, 883 cm^{-1}, 564 cm^{-1}, and 431 cm^{-1}. The peak indicates the stretching vibration of the O-H group at 3399 cm-1, and the peak indicates the metal-oxygen ZnO stretching vibration mode at 564 cm-1. Peaks located at 2925 cm-1 and 3399 cm-1 are indicative of hydroxyl compound stretching vibrations. The nitrate peak in the capping agent is indicated by the absorption peaks at 1625 cm-1[12]. The absorption peaks between 2,300 and 2,400 cm-1 indicate the CO2 mode[13]. There are absorption peaks at 3428 cm-1, which progressively disappear[14]. The steep peak at 1123 cm-1 is caused by the bending vibration of the C-H plane [15]. The alcohol in-plane bend or vibration caused by primary and secondary causes the peaks at 1383.7 cm-1.

Table 2. FTIR bands and their assignments in ZnO nanoparticles.

Sr. No.	Absorbent peak position (wave number) cm^{-1}	Functional group
1.	3399	O-H group, stretching vibration
2	2925	O-H stretching vibration
3	1625	O-H bending vibration
4	1383	primary, secondary alcohol in-plane bend or vibration
5	1103	C-H plane bending vibration
6	883	Nitrate peaks
7	564	metal-oxygen (ZnO stretching vibrations)
8	431	Zn–O stretching vibration mode

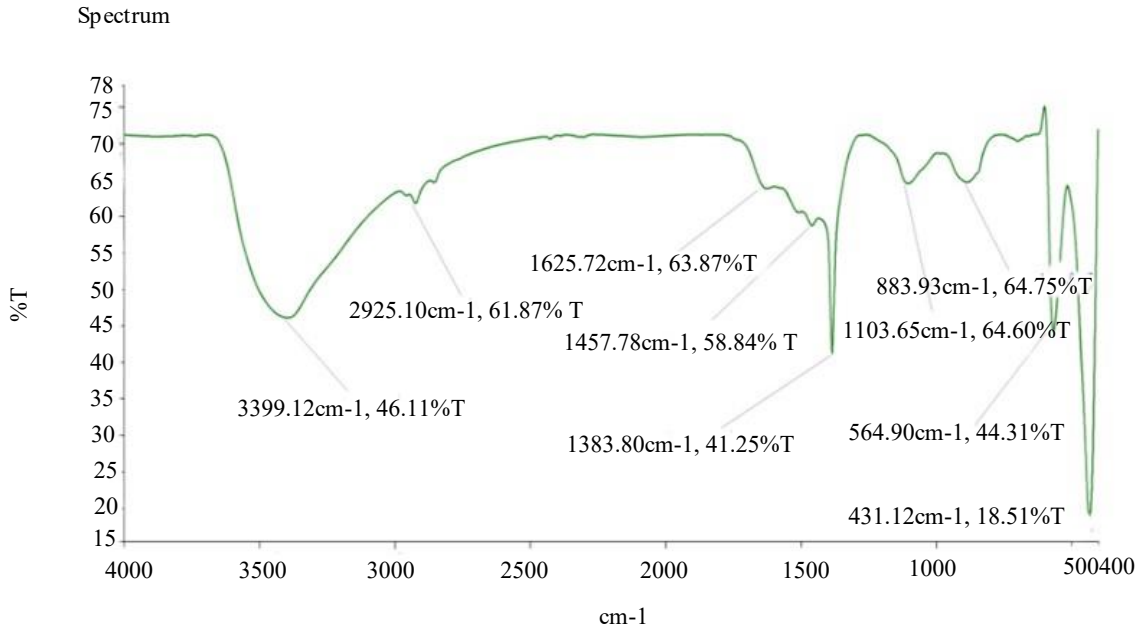

Figure 5. FTIR spectra of synthesized ZnO Nanoparticles.

EVALUATION OF PROPERITIES OF PROPERTIES OF FABRICATED NANOCOMPOSITES OF RUBBER

Cure Characteristics of Rubber Composite

The curing and torque studies were followed with an oscillating disc rheometer at a temperature of 150°C and an oscillating arc of 3º and the results are presented in Table 3. The cure rate index (CRI) was calculated from the following expression[16].

$$CRI = \frac{100}{(t90 - t2)}$$

Where, t_{90} is the optimum cure time, which is the time corresponding to the torque value calculated using the expression, $M_L+0.9(M_H+M_L)$, M_H and M_L being the maximum and minimum torque.

Table 3. Cure characteristics of nano ZnO/ rubber composites with different formulations.

phr	Cure characteristics of nano ZnO/ rubber composites						
	T_{S2}	Tc_{90}	Tc_{90}-T_{S2}	*Cure Rate index (min)*	M_L	M_H	M_H-M_L
0.5	2.63	10.05	7.42	13.47	28.16	98.49	70.33
1	2.78	9.2	6.42	15.57	25.78	109.71	83.93

2	2.8	9.58	6.78	14.74	26.78	104.71	77.93
4	2.48	10.53	8.05	12.42	27.11	102.43	75.32
6	2.25	11.25	9	11.11	28.28	100.27	71.99

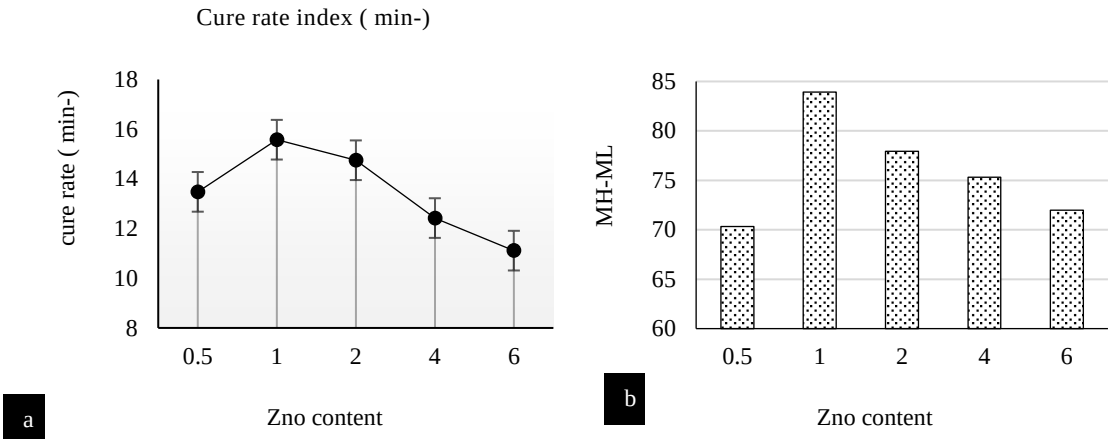

Figure 6. (a)Impact of the Nano ZnO Content on Cure rate index (min^{-}) (b) Torque Difference of nano ZnO Composites.

The cure characteristics and torque report results are shown in Figure 6. The torque difference (M_H-M_L) of nano ZnO/ rubber composite at 1 phr is maximum the value was found to be 83.93(lb). In these results we can see the when ZnO amount is increased the cure rate index and torque difference are increased continuously. Nano ZnO of 1phr as an effective filler for better performance of elastomeric rubber composites. The creation of crosslinks within the rubber matrix frequently occurs more quickly when the cure rate index and torque difference are greater. A small amount of nano ZnO is a more effective cure activator and crosslinking agent during rubber vulcanization than traditional ZnO[16][17].

Tensile Strength

Three dumbbells were tested for each compound, and the average result was used. Each sample's standard deviation was computed. Nano ZnO increased the vulcanizates' tensile energy without altering their break-in elongation.

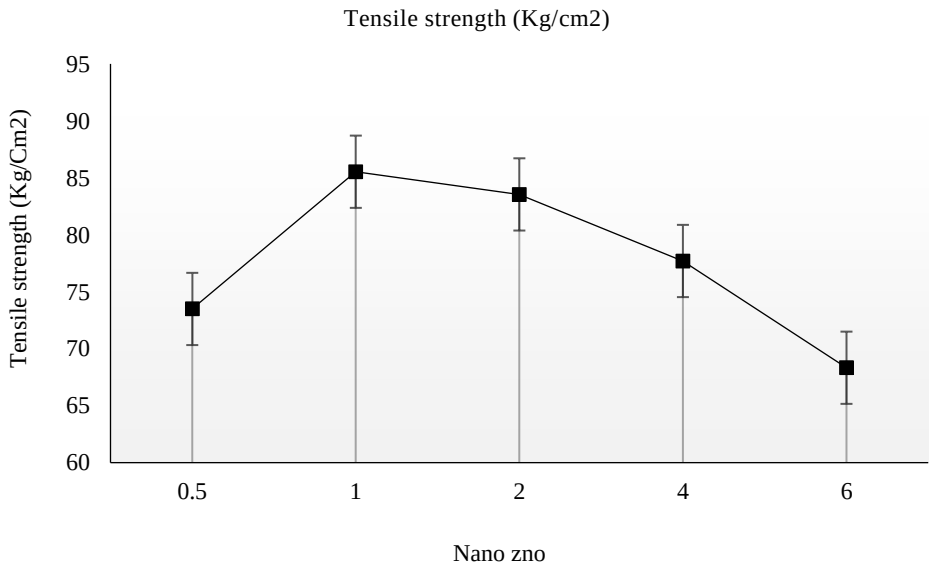

Figure 7. Impact of nano ZnO content on tensile srength.

The mechanical properties of vulcanized rubber are directly influenced by the crosslink density and structures[18]. The tensile strength was increased and it had a maximum value at 1 phr zinc oxide shown in Figure 7 that approximately value was 83.54 Kg/cm^2. When increasing the amount of cure activator the tensile strength was decreased gradually. These improvements are attributed to the effective reinforcement provided by the ZnO nanoparticles, which enhance the cross-linking density within the rubber matrix at 1 phr. This could be the outcome of sepiolite, a nanofiller, working in concert with carbon black, a conventional filler [19].

Elongation

The capacity of a rubber compound to stretch without breaking is known as elongation. It is equivalent to the ratio of the final length to the initial length.

$$E_L = \frac{L - L^\circ}{L} \circ \%$$

Where E_L is elongation, L is the final length and L° is the initial length.

Figure 8 illustrates the difference in elongation percentage of nano ZnO at different phr. The elongation at break decreased as zinc oxide level increased due to the relationship between cross-link density and zinc oxide level. Because of the extreme stretching in the nano ZnO/ rubber composites. As we increase the loading of nano zinc from 4 to 6phr, the brittleness of the rubber matrix increases. Elongation has decreased because rubber becomes brittle and breaks quickly. A corresponding increase in the efficiency of crosslink formation results in less elastic material and a decrease in elongation at break. elongation is the extension caused by tensile force between benchmarks [20].

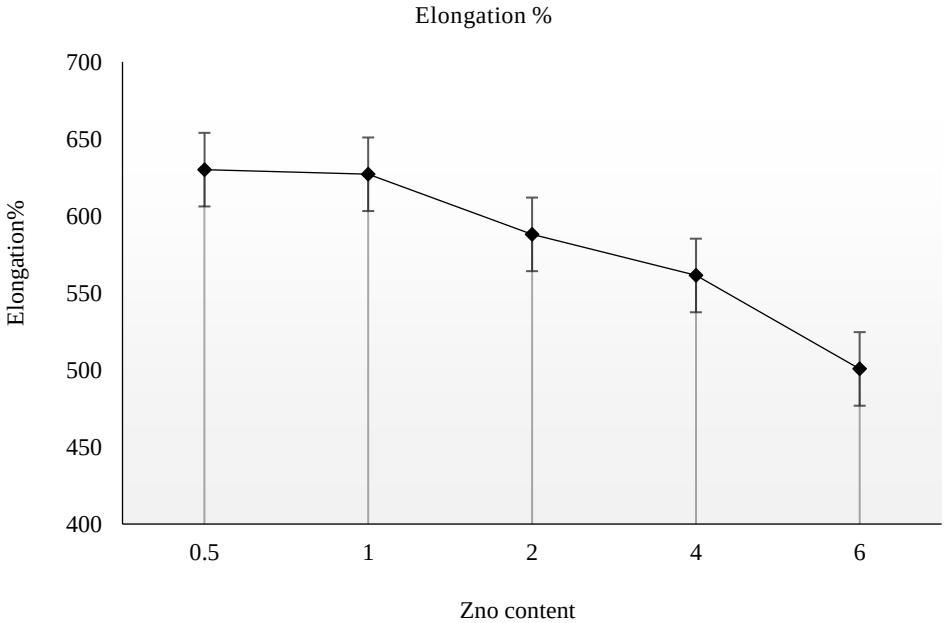

Figure 8. Impact of Nano ZnO Content on elongation%.

Hardness Test

The hardness of a material is determined by how resistant its surface is to being indented. The influence of different loadings of nano ZnO in the rubber matrix is given in Figure 9. Hardness increased as the concentration of zinc oxide increased, the values obtained with nano ZnO. The permeability of rubber composite is reduced by the cross-links, which is why it increases as the cross-link density

increases. The interaction between the fillers and matrix is enhanced by the nanoparticles present in the composite[21]. Hardness rises as zinc oxide levels rise because of increased crosslink density formation and crosslink efficiency. A multitude of investigations concerning the activation processes have revealed that ZnO reacts with different additives [22].

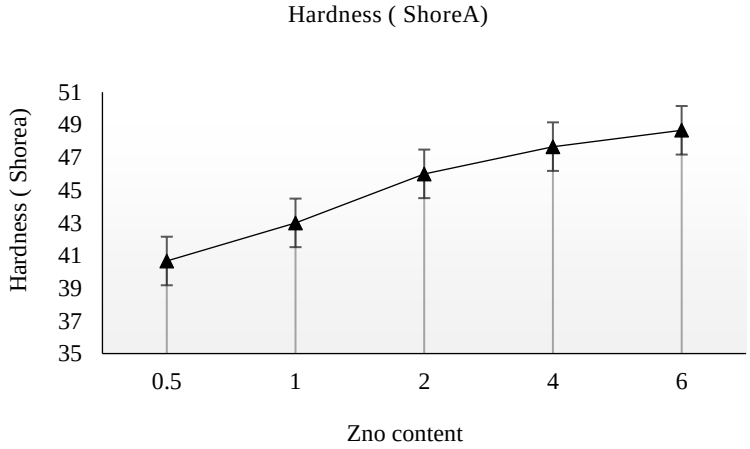

Figure 9. Impact of the Nano ZnOContent on Hardness.

CONCLUSIONS

In this study, we have synthesized ZnO nanoparticles through the precipitation method characterized their structural and morphological properties, and evaluated their performance in rubber composites. The synthesis process yielded ZnO nanoparticles with a high degree of purity and uniformity, as confirmed by X-ray diffraction (XRD) scanning electron microscopy (SEM), and Fourier Transform Infra-Red (FTIR) Spectroscopy. The particles exhibited an average size of approximately 29.78±5 nm, with a distinct hexagonal crystal structure. The incorporation of ZnO nanoparticles into rubber composites demonstrated notable influence on cure characteristics. The cure rate index was maximum in 1 phr of nano/ rubber is approximately 15.57 per minute which is the maximum for other (2-6) phr loadings. Tensile strength also has a maximum value of tensile strength at 1 phr loading which means that the interaction of nano ZnO and rubber matrix is better at 1 phr. As we increase the level of zinc oxide, the interaction/crosslinking between zinc oxide and rubber matrix decreases.

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