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THE EFFECT OF CURE ACTIVATOR ZINC OXIDE NANOPARTICLES ON THE MECHANICAL BEHAVIOR OF POLYISOPRENE RUBBER

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Abstract

Zinc oxide is an effective material due to its unique physical and chemical properties. The present work use of a limited amounts of zinc oxide nanoparticles produced by sol-gel process as an alternative to conventional zinc oxide and investigated the effects of this material on the mechanical behaviour of rubber recipes including cis-Polyisoprene rubber vulcanized by sulphur. Results showed the possibility of using nanoparticles of zinc oxide produced by chemical method in smaller quantities to achieve better results than the conventional zinc oxide used with rubber recipes especially (0.3 and 0.4 pphr). Results of Aging and Swelling test confirm the validity of the use of this material and the results showed significant improvements in these characteristics. Tensile strength about 9.8, 11.2, 13.9, 15.4 and 15.7 MPa were observed at 0.1, 0.2, 0.3, 0.4 and 0.5 pphr respectively compared to 12.6MPa was observed at 4 pphr conventional ZnO. Also, the reduction ratio were 95%, 95%, 80%, 73%, 70% and 79% at aging time reach to 120h for the recipes 4 pphr (conventional), 0.1, 0.2, 0.3, 0.4 and 0.5 respectively, while the swelling characteristics shows better resistance at 0.3 and 0.4 recipes pphr ZnO NPs. in toluene at room temperature. Current work supports the trend towards reducing the amount of zinc oxide used in rubber compounds as a cure activators agent.

Keywords: Aging, Cure activator, Polyisoprene rubber, Sol-gel process, Swelling, Zinc oxide.

1. Introduction

Today, nanotechnology works in various fields of science by operating materials and devices using different nanometer-scale techniques. Nanoparticles are part of nanomaterial's known as individual molecules with a diameter of 1-100 nm. Recently, nanoparticles have been used in new and sophisticated applications such as biological, optical and electrical applications as well as in energy and data storage. Nanoparticles have unique properties and multiple benefits as a result of having small size [1].

There are different kinds of nanoparticles reported in previous studies, for example, metal and polymeric nanoparticles. Among these metal particles of nanostructure is one of the most versatile materials, given their various properties and functions. The most preferred among different oxide metal particles, zinc oxide ,nanoparticles are of particular importance due to a wide range of applications, for example, gas sensor, chemical sensors, biological sensors, cosmetic storage, optical and electrical devices, Solar cells, and drug delivery [2].

Nanoparticles zinc oxide can be synthesized by various ways including sol-gel processing, chemical precipitation, mechanical milling, Organic metal synthesis, microwave method, thermal pyrolysis of spray, thermal evaporation and chemical mechanical synthesis [3].

The current study focuses on the preparation of zinc oxide nanoparticles by sol-gel process shows the difference in particle size, morphology and the elemental composition of the nanoparticles obtained by this method. Also, study the ability of these particles to compound with rubber recipes in the engineering applications was discussed. To the best of our knowledge, there are no other work using ZnO NPs. with cis-Polyisoprene rubber instead of conventional formulations with specific ratio and size towards reducing the amount of conventional zinc oxide that used in rubber compounds as a cure activators agent.

2. Materials and Methods

2.1. Preparation of ZnO nanoparticles (NPs.) by sol-gel method

Zinc oxide molecules were manufactured using sol-gel method using zinc acetate and methanol in synthesis of zinc oxide NPs (Fig. 1). 16 g of zinc acetate was dissolved in 112 mL of methanol. After 10 minutes of magnetic mixing at room temperature, the solution result was subject to gelation at 80 ºC with continuous stirring for 5 hours, and zinc nanoparticles were obtained in powder form. Resulting powder was annealed at 450 ºC for 6 hours [4].

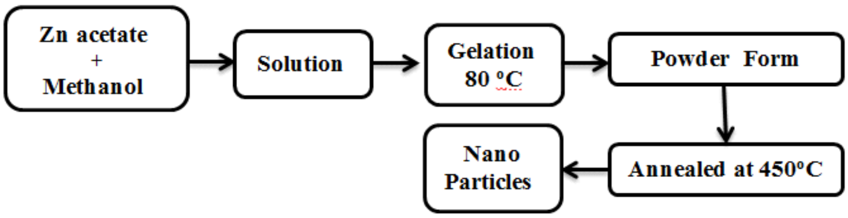


Fig. 1. Scheme sol-gel method.

2.2. Morphological characterize

Morphology of the ZnO NPs. was examined with the help of scanning electron microscope (SEM) machine.

2.3. Optical study

Optical, characters of the synthesized zinc oxide nanoparticles were studied by analyzing the ultraviolet visible (UV-Vis). spectrometer using spectrophotometer, Fourier-transform infrared spectroscopy (FTIR) curve for ZnO NPs. was obtain by used FTIR (SHIMADZU), spectrum. Also, XRD (X-ray diffraction) was studied. The crystal size of ZnO NPs. was calculate by scherror Eq. (1):

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

where D: crystal size, λ: X-ray wavelength β: full width at half maximum, K: is scherror constant, and θ: Bragg diffraction angle.

2.4. Mechanical and physical tests

Mechanical behavior was evaluated during this study which is based on comparing between recipe that use conventional zinc oxide and new recipes with different ratio of zinc oxide nano particles prepared by sol-gel method as mentioned previously. All the rubber recipes were prepared with different types of materials through two stage master and final batch with same ratio in part per hundred of rubber (pphr) such as (IR), Stearic-Acid, Carbon Black (C.B.) N550, Anti-Ozonant (IPPD), Anti-Oxidant (TMQ), Paraffin Wax, Dutrex Oil in addition to CBS and Sulphur as shown in Table 1. Cis-Polyisoprene has properties similar to that of natural rubber, with insensitivity to temperature changes, good tensile strength and low resistance to abrasion.

Table 1. Standard and modified recipes.

No.	Material	Standard (RS)	R1	R2	R3	R4	R5
	Master Batch	Loading (pphr)					
1	**IR (rubber)**	100	100	100	100	100	100
2	**ZnO**	4	0	0	0	0	0
3	**ZnO NPs.**	0	0.1	0.2	0.3	0.4	0.5
4	**Stearic-Acid**	2	2	2	2	2	2
5	**C.B. (N550)**	51	51	51	51	51	51
6	**IPPD**	1.75	1.75	1.75	1.75	1.75	1.75
7	**TMQ**	1	1	1	1	1	1
8	**Wax**	3	3	3	3	3	3
9	**Dutrex Oil**	8.5	8.5	8.5	8.5	8.5	8.5
	Batch						
10	**CBS**	0.500	0.500	0.500	0.500	0.500	0.500
11	**Sulphur**	2.000	2.000	2.000	2.000	2.000	2.000

The physical and mechanical tests were conducted during this study as the following:

2.4.1. Tensile test

Dumbbell-shaped specimens were prepared and the average of the three measurements shall be used with thickness (2.0±0.2 mm) at room temperature (23 ± 2 °C) and relative humidity at (50 ± 5 %) and condition the specimens for at least 24 hr. prior to testing as described in ASTM D412 by Monsanto T10 Tensometer machine [5, 6].

2.4.2. Ageing test

Dumbbell-shaped specimens prepared as described in test methods ASTM D 412 and their form for three test specimens at (70±1°C) with pressure of oxygen supplied to the aging chamber shall be (2100±100 KPa) according to ASTM D572 for each period of testing procedure 24 h, 48h, 72 h, 96 h, 120 h [7, 8].

2.4.3. Swelling test

During this test, the amount of change in weight of the rubber specimens due to immersion in toluene with Dumbbell-shaped specimens prepared as described in test methods ASTM D 412 at room temperature (23+ 2 ºC) at absence of direct light for different periods 24 h, 48h, 72 h, 96 h, 120 h in toluene and according to ASTM D3616 [9, 10]. The swelling index (SI) was evaluated according to Eq. (2) [11, 12]:

$$SI = \frac{W_2 - W_1}{W_1} \tag{2}$$

where W_1: the initial mass and W_2: the mass of wet specimens after immersion in toluene.

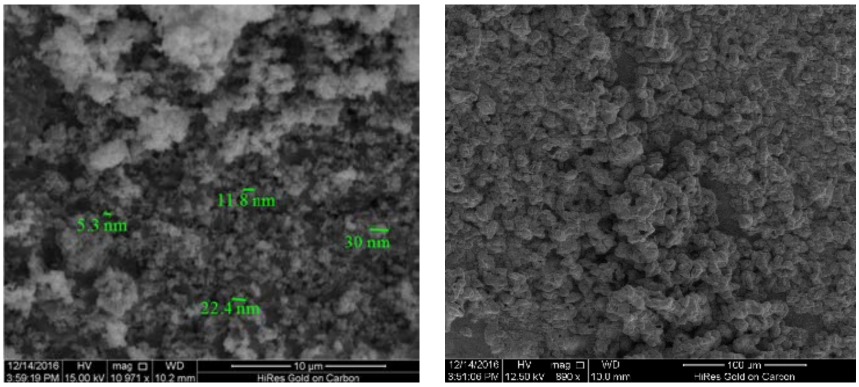
3. Results and Discussion

3.1. Synthesis of zinc oxide nanoparticles

The formation of zinc oxide NPs. was found to be successful by formed white powder in the end of synthesis process [13].

3.2. SEM, analysis of zinc oxide nanoparticles

Size and structure of synthesized nanoparticles was analysis by SEM image and used I-image J program for calculated the size of nanoparticles. These were revealed visualize the size and shape of zinc oxide nanoparticles. Figures 2(a) and (b) show different aggregation of spherical shape of zinc oxide nanoparticles with size 5.3 to 30nm and this result compatible with Ramesh et al. [14] and Kulkarni et al. [15].



a) higher resolution ZnO NPs. **b) Zinc oxide NPs.**

Fig. 2. Zinc oxide NPs image by SEM.

3.3. Optical study

The UV spectrum of the sample is shown in Fig. 3. It is apparent that absorbs the radiations range up 330 nm. The radiations of visible spectrum are transmitted by the nanoparticles of Zinc oxide. Paul and Ban [16] reported that the peak was found at 370 nm which was the characteristics of ZnO NPs formation. Also, Santhoshkumar et al. [17] explained that Optical properties of ZnO NPs were characterized based on UV absorption spectra with the wavelength range of 300-500 nm.

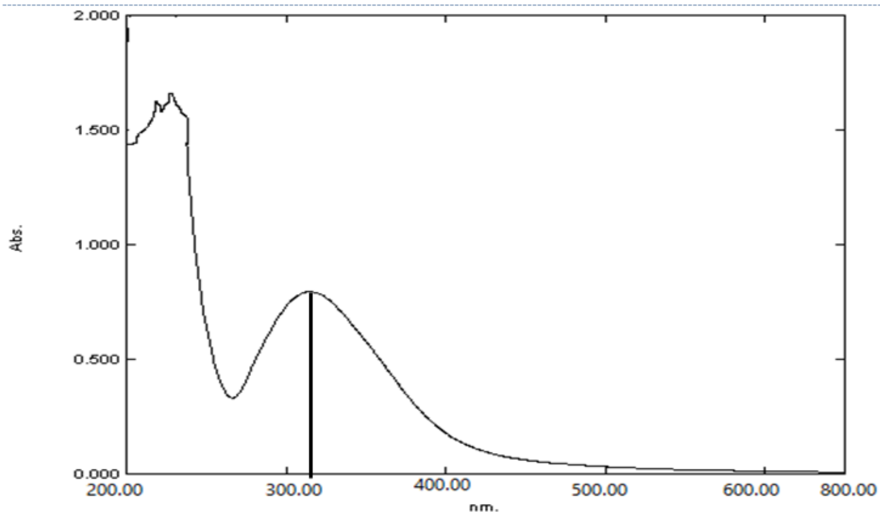


Fig. 3. UV spectrum of ZnO NPs (sol-gel method).

FTIR curve for ZnO NPs. in Fig. 4 shows the peaks from 1500 to1700 cm^{-1}, from 2,300 to 2,750 cm^{-1}, and in 3000 cm^{-1} are the functional groups corresponding to the C-O, C-H and O-H respectively. The presence of O-H represents the presence of water molecules on the surface of ZnO NPs [18].

X-ray diffraction reveals its properties through X-ray diffraction graph as shown in Fig. 5. There are four peaks according to ZnO zincate phase. A number of peaks were observed due to impurities, which represented that high-purity zinc oxide was obtained. The peak has also been expanded which means that the particle size is too small [19]. The average size according to scherror equation was found to be equal (13.30).

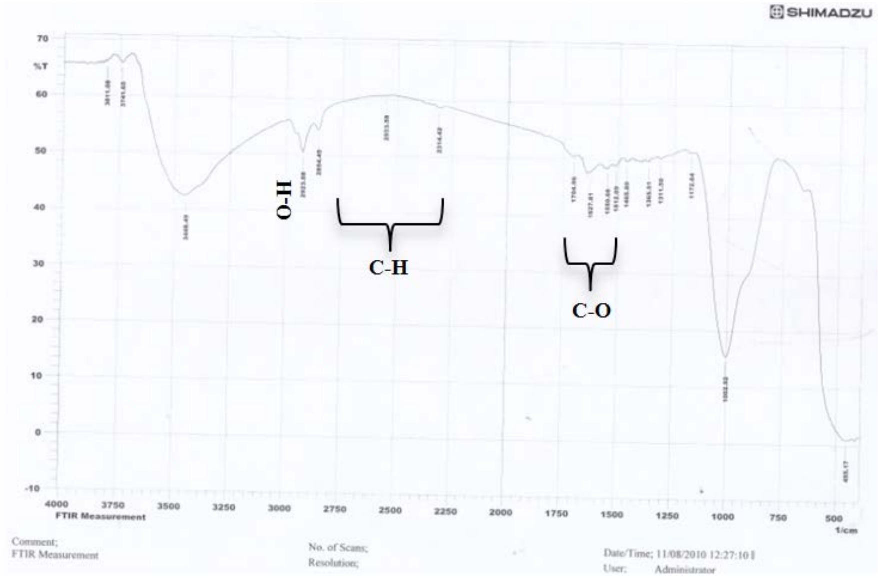


Fig. 4. FTIR spectrum of ZnO NPs (sol-gel method).

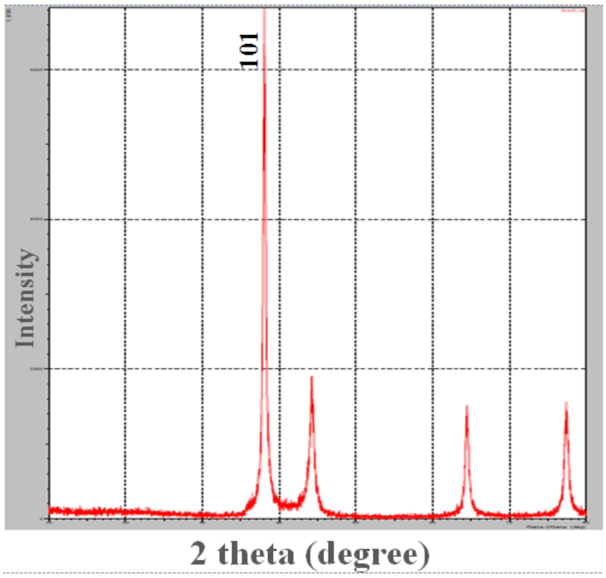


Fig. 5. XRD of ZnO NPs (sol-gel method).

3.4. Mechanical and physical tests

3.4.1. Tensile test

The tensile strength results of (IR) with cure activator agent (conventional ZnO) 4 pphr that used in rubber compounds that appear at 0 pphr and ZnO NPs. 0.1 to 0.5 pphr loading as shown in Fig. 6. The average value of the tensile strength was increased by about 25%. At the zinc oxide nanoparticles with average size 5.3 to 30nm, an excellent tensile strength of 9.8, 11.2, 13.9, 15.4 and 15.7 MPa were observed at 0.1, 0.2, 0.3, 0.4 and 0.5 pphr respectively and a remarkable tensile strength of 12.6MPa was observed at 4 pphr conventional ZnO quantity. However, reducing the size of particles to the nanometer increases the surface area and that led to a larger amount of matter is in contact with the surrounding material and this improves the catalysis. Also, led to an increase in cross-linking density of the rubber recipes. Therefore, ZnO nanoparticles can be used to reduce the amount of ZnO that use in rubber conventional formulations [20, 21].

The increasing of ZnO NPs. to 0.5 pphr may be did not provide significant differences from its previous values 0.4 pphr, perhaps because of the rubber recipes taken enough for an instantaneous reaction with stearic acid to produced zinc sulphide where the function of stearic acid is to solubilize the zinc oxide and increase in the amount of zinc sulphide produced [22] and remain the rest of the material as a filler, while the few quantities such as 0.1 pphr NPS. maybe do not support this interaction.

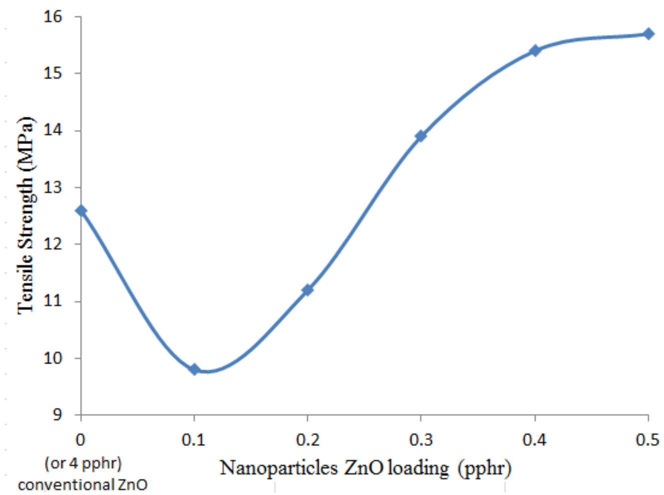


Fig. 6. Tensile test results.

3.4.2. Aging test

The tensile strength of the rubber recipes after aging testing was lower than before it with a reduction ratio 95%, 95%, 80%, 73%, 70% and 79% at aging time reach to 120h for the recipes RS, R1, R2, R3, R4 and R5 respectively as shown in Fig. 7. This was maybe caused by heating the samples for different periods. The heat may be caused damage the crosslinking rubber chains and growing degradation of the long-chain molecules, which led to deterioration in the mechanical properties of the vulcanized rubber recipes such as tensile strength and elongation at break and this led finally to increase the stiffness of the recipes [23, 24].

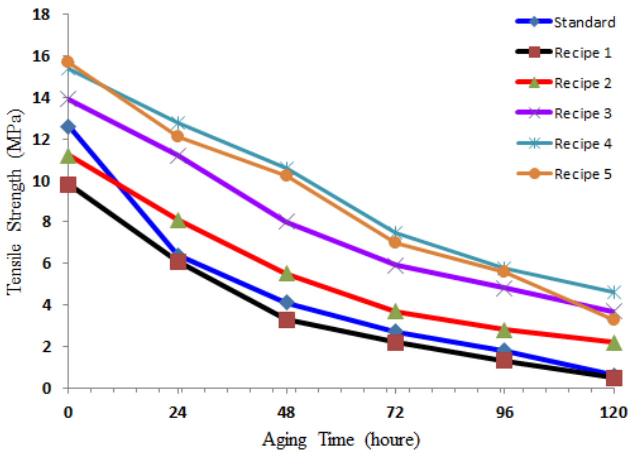


Fig. 7.Tensile strength at various aging times.

3.4.3. Swelling test

Moreover, the tensile strength of the rubber recipes after swelling testing was lower than before this process with a reduction ratio 70%, 72%, 68%, 59%, 61% and 61% at swelling time reach to 120h for the recipes RS, R1, R2, R3, R4 and R5 respectively as shown in Fig. 8. The swelling characteristics of vulcanizes rubber in toluene at room temperature shows better resistance at R3 and R4 recipes with 0.3 and 0.4 pphr ZnO NPs. respectively, with more restrictions for the solvent to penetrate through this recipes and greater crosslink density. While recipes that using conventional zinc oxide and low ratio of ZnO NPs gave less resistance to solvent penetration, possibly because of poor generation of crosslinking [25].

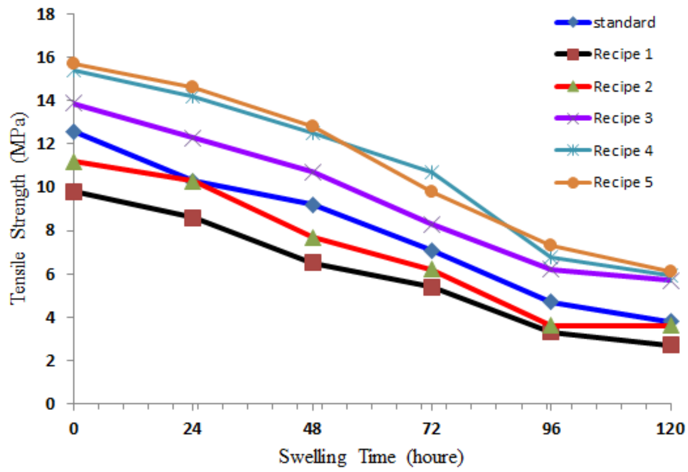


Fig. 8.Tensile strength at various swelling times.

4. Conclusions

An investigation has been made of the effects of ZnO NPs that manufacturing by chemical method on the mechanical behaviour of polyisoprene rubber compounds and found:

- The low ratio of the ZnO NPs. played in obtaining a homogenous mixture resulting from good dispersion in the rubber chains.
- The yield of sol-gel process is very active to produce ZnO NPs. to supports the trend towards reducing the amount of zinc oxide used in rubber products as a cure activators agent in addition to the reduction in time of vulcanization process.
- Zinc oxide can be replaced by significantly lower amounts of ZnO NPs. with improvements in the properties of tensile, aging and swelling properties and the acceptable results for these tests were at values of 0.3 and 0.4 pphr, where the improvement was about 25% compared with conventional zinc oxide at 4 pphr.

Finally, the present study recommends the study of other methods of producing nanoparticles and comparing their effectiveness with the results of the current study.

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