

## ARTICLE

# SYNTHESIS OF THE CoO.CaO/ZnO CORE-SHELL NANOPIGMENT AND INVESTIGATION OF ITS EFFECTS ON THE PROPERTIES OF RUBBER COMPOUNDS BASED ON THE ACRYLONITRILE BUTADIENE ELASTOMER (NBR)

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## ABSTRACT

synthesis of the core-shell nanopigment with two different proportions of shell (1CoO.3CaO/ZnO and 3CoO.1CaO/ZnO) and its effects as an activator on the properties of the acrylonitrile butadiene elastomer (NBR) were studied. To characterize the nanopigments, XRD, SEM, and TEM analyses were used. Also, 15 phr of the nanopigments with two different proportions, as mentioned before, were added to the elastomer base (NBR). The results obtained from the X-ray diffraction (XRD) confirmed the formation of desired phases, and the average particle sizes of particles for two proportions of 1:3 and 3:1 were reported to be 19 and 31.27 nm, respectively, using the Scherrer equation. Also, the images received from the SEM analysis proved the spherical shape of the particles. The approximate sizes of the particles for two proportions were within the ranges of 47.1–100 and 41.3–98.9 nm, respectively. The images obtained from the TEM analysis showed the formation of nanometer shells on the core surface (ZnO). Owing to the loading of the newly synthesized nanopigments with different proportions on the nitrile elastomer (NBR), there is a marked improvement of the rheological and physicochemical properties compared to the reference sample. The results confirmed the booster role of the new nanopigments.

## INTRODUCTION

Polymer compounds are widely used in packaging, transportation, and automotive industries. Therefore, it is vitally important to improve their properties and qualities. One of the most effective factors of the physical and mechanical properties of rubber compounds is the use of fillers [1]. Fillers are classified into two types: soot and color [2]. Use of inorganic fillers with outstanding properties, such as high chemical resistance, environment-friendly, and reduced price in the polymer industry, is significant [3]. In fact, fillers improve the tensile strength and modulus; they reduce the cost of rubber compounds. This specific effect can be attributed to the chemical state of the filler surface, the shapes and sizes of particles, and their specific surface [1]. Zinc oxide (ZnO) has many applications in most industries; these include the production of ceramic pigments and electrical and optical materials [4]. A most common use of ZnO is in the polymer industry. The white color, the small size of particles, acid acceptor, and adaptability with organic and inorganic compounds are the reasons for the wide-ranging use of ZnO. It is generally used in the polymer industry as an activator, booster, and pigment [1]. The new approach applied by different industries to produce their products is the use of hybrid particles or the core shell. These particles have wide applications in the pharmaceutical industry (drug delivery), chemical engineering, biology, and optics [5]. In general, core-shell particles contain more than one chemical sedimentary component [6]. The core is usually chosen as a low-cost factor that contains 80%–85% 'per cent' of compounds. This factor can be covered by a shell that includes only 15%–20% 'percent' of pigments. Generally, hybrid compounds have unique properties compared to the time when they are used separately [7]. As a result, different studies have been carried out by researchers. One of these studies was conducted by Ahmed and El-Nashar in 2013, where the effects of ZnO/phosphate core-shell pigments on the properties of SBR/EPDM synthetic compounds with a proportion of 50:50 were investigated [1]. The results confirmed the effective role of the new pigments on the physical–mechanical properties and rubber compounds based on the SBR/EPDM in comparison with the commercial samples of pigments. Also, the high concentration of magnesium compared to the calcium concentration in the shell containing phosphate shows better properties in synthetic compounds. Also, the effects of CoO.MgO/Kaolin core-shell pigments with two different sizes, micro and nano, on the properties of SBR rubber were studied by Ahmed et al. in 2011[6]. Kaolin was considered as a core, while cobalt and magnesium oxides were chosen as a shell. The results showed that loading 6 phr of the nanopigments improve the physical–mechanical and dielectric properties in the styrene butadiene elastomer. The optimum loading for the micro-pigments was 30 phr. In 2013, El-Nashar et al. studied the effects of new ferric-kaolin pigments on the rheological, physicochemical, and magnetic properties of rubber compounds based on nitrile butadiene [7]. The results illustrated that by increasing the loading to 50 phr, the mechanical properties of rubber compounds based on NBR rises and then decreases. Hardness and magnetic properties considerably increase by loading the new core-shell pigments based on the nitrile elastomer compared to the reference sample. In 2015, another study was conducted by El-Sabbagh and Ahmed to investigate the productivity of styrene-butadiene rubber composites using kaolin covered by metal oxide pigments as a shell [8]. The results depicted that inorganic core-shell pigments improve cooking and the physical–mechanical properties as well as the tensile strength of rubber compounds based on the SBR elastomer. The merits of this method were the compatibility of inorganic pigments with the environment and the low-cost procedure. In 2015, Ahmed et al. synthesized the new kaolin–ferric core-shell pigments with the anticorrosion and environmental-friendly properties [9]. According to their results, the new kaolin–ferric core-shell pigments have an appropriate function in terms of corrosion in comparison with the common ferric pigments. Owing to their

### KEY WORDS

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environmental-friendly properties and low-cost procedure, the new pigments can be a good choice for color formulation, booster fillers in rubbers, ceramic composites, and electric nonconductors. The most important point in their results is the possibility that hybrid pigments could be replaced with other dangerous pigments such as chromates with the same performance. In 2015, Mao et al. synthesized  $\text{Ce}_2\text{S}_3@\text{ZnO}$  with the core-shell structure and investigated its application as an inorganic and nontoxic pigment [10]. In their research, owing to the diffusion of hydrogen sulfide ( $\text{H}_2\text{S}$ ) by cerium selenide ( $\text{Ce}_2\text{S}_3$ ) and the resultant environmental problems, cerium selenide was covered with a uniform layer of ZnO. The results indicated that a uniform layer of ZnO with a thickness of 40 nm was covered on the core surface via a simple and low-cost method. The presence of a protective layer of ZnO prevented the diffusion of  $\text{H}_2\text{S}$  and hence the use of the new core-shell method resulted in the production of nontoxic, environment-friendly, and odorless pigments that have thermal stability. In 2013, Mark et al. studied the application of the core-shell theory in reducing the use of ZnO on the nitrile elastomer [11]. According to their research, which is now under review and based on the Europe Union Theory regarding the pollution of ZnO, all industries try to reduce the use of ZnO. However, ZnO plays an important role in the vulcanization process of rubber compounds. In this research, the effects of green core-shell nanopigments with different proportions of shells ( $1\text{CoO}.3\text{CaO}/\text{ZnO}$  and  $3\text{CoO}.1\text{CaO}/\text{ZnO}$ ) on the physical-mechanical properties and cooking rubber compounds based on the nitrile elastomer were investigated. Also, the boosting level of new nanopigments was studied. It should be mentioned that ZnO was considered as a core that contains just 80% 'percent' of the compound in the new nanopigments and covered with a shell of cobalt and calcium oxide with proportions of 1:3 and 3:1. The shell only includes 20% 'percent' of nanopigments.

## MATERIALS AND METHODS

The chemicals employed in the synthesis of core-shell nanopigments are as follows:

Zinc oxide (ZnO) with 99% purity made by Daejung Company in South Korea, calcium nitrates and cobalt nitrates with 99% purity made by Merck Company in Germany, ammonia with 25% purity made by Merck Company in Germany, ethanol with 99% purity made by Merck Company in Germany.

The materials employed in the synthesis of rubber compounds based on the NBR are as follows:

Acrylonitrile butadiene (33%) made by LG Company in South Korea, stearic acid made by Chem Acid Company in Malaysia, CBS made by Lanxess Company in Belgium, sulfur with 99% purity made by Tesdak Company in Iran, ZnO made by Shokouhieh Company in Iran, dioctyl phthalate (DOP) made by LG Company in South Korea.

The devices employed in the characterization of core-shell nanopigments are as follows:

Electric furnaces (the BATEC-PC-21 model) made in Taiwan, the X-ray diffraction (XRD) device (the STOE-STIDY-MP model) made in Germany, the scanning electron microscope (SEM) device (the KYKY-EM3200 model) made in China, the transmission electron microscope (TEM) device (the EM10C-100KV model) made by ZEISS Company in Germany.

The devices employed in testing rubber compounds based on the NBR elastomer are as follows:

Two-roller mill made by WSMCO.LTD Company in Taiwan, the rheometer device (the MDR-HIWA900 model) made by HIWA Company in Iran, the laboratory hydraulic press (the PTP60 model) made in Iran, the puller (the UNIVERSAL-M350-5KN model) made by TESTOMETRIC Company in Iran.

**Synthesis of core-shell nanopigments with two different proportions of the shell:**

To synthesize  $1\text{CoO}.3\text{CaO}/\text{ZnO}$  and  $3\text{CoO}.1\text{CaO}/\text{ZnO}$  core-shell nanopigments, the co-precipitation method was used. It should be mentioned that the percentage of core and shell considered for nanopigments were 80% and 20%, respectively. First, certain amounts of cobalt nitrate and calcium nitrate along with ZnO were dissolved in water. To create an alkaline media, ammonia was added. Then, the solution was stirred using a magnet for 6–12 h. The obtained precipitate was filtered, heated in an oven, and finally, calcined in an electric furnace with an average slope of  $20\text{ }^\circ\text{C}\cdot\text{min}^{-1}$  within a temperature range of 600–1000  $^\circ\text{C}$  for 1–12 h. To characterize the nanopigments, X-ray diffraction, SEM, and TEM analyses were performed. The achieved results have been discussed in the Results and Discussion section.

**Synthesis of rubber compounds based on the NBR:**

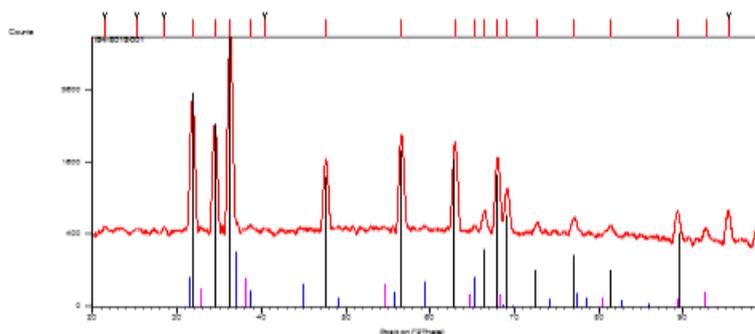
The synthesis of rubber compounds was accomplished based on the new formulation presented in [Table 1]. In this research, a sample was considered as a reference sample without nanopigments, and two other samples were loaded by the new nanopigments. First, the components were processed on the two-roller mill device within a temperature range of 75–80 °C in two steps. During the synthesis of the mixture, the temperature, time, and shape of sections were exactly controlled. To start the synthesis of rubber compounds, the elastomer, activators, fillers, emollients, and antioxidants were processed by the two-roller mill device. In the second step, the accelerator and sulfur were added to the mixture because early use of the two compounds disrupts the cooking process. In this study, owing to the absence of soot, the new core-shell nanopigments were added to the mixture after adding the activator. The most significant thing in the synthesis of rubber compounds is a uniform distribution of nanopigments via the core-shell method, which is an important advantage in using new nanopigments. After preparing the mixture, the samples were kept at room temperature for 24 h, pressed under by the hydraulic press device, and baked under the appropriate temperature. Next, the tensile and cooking tests were carried out. The obtained results have been discussed in the Results and Discussion section.

**Table 1:** The selected formulation for the synthesis of rubber compounds

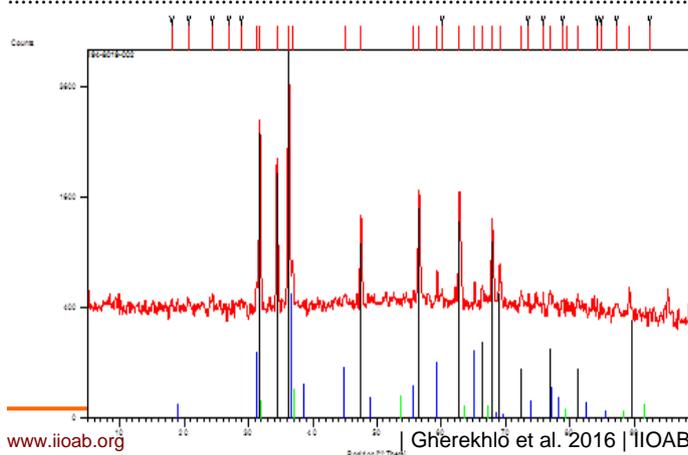
Chemicals	Z <sub>b</sub>	Z <sub>1:3</sub>	Z <sub>3:1</sub>
NBR	100	100	100
S.A (Stearic acid)	1.5	1.5	1.5
N-Cyclohexyl-2-benzothiazole Sulfonamide (CBS)	1.7	1.7	1.7
S	1.5	1.5	1.5
ZnO	5	5	5
Diocyl phthalate (DOP)	3	3	3
1CoO.3CaO/ZnO	-	-	15
3CoO.1CaO/ZnO	-	15	-
Values based on phr (Part per Hundred parts of Rubber)			
Z <sub>b</sub> : The reference sample without the nanopigments. Z <sub>1:3</sub> : The sample containing 15 phr of 1CoO.3CaO/ZnO nanopigment. Z <sub>3:1</sub> : The sample containing 15 phr of 3CoO.1CaO/ZnO nanopigment.			

## RESULTS and DISCUSSION

The XRD analysis was employed to investigate the crystal structure of the synthesized core-shell nanopigments. The analysis was carried out at 25 °C in the presence of a copper lamp. The XRD patterns of 1CoO.3CaO/ZnO and 3CoO.1CaO/ZnO core-shell nanopigments have been illustrated in [Fig. 1] and [Fig. 2].



**Fig. 1:** The XRD pattern of the 1CoO.3CaO/ZnO nanopigment.



**Fig. 2:** The XRD pattern of the 3CoO.1CaO/ZnO nanopigment.

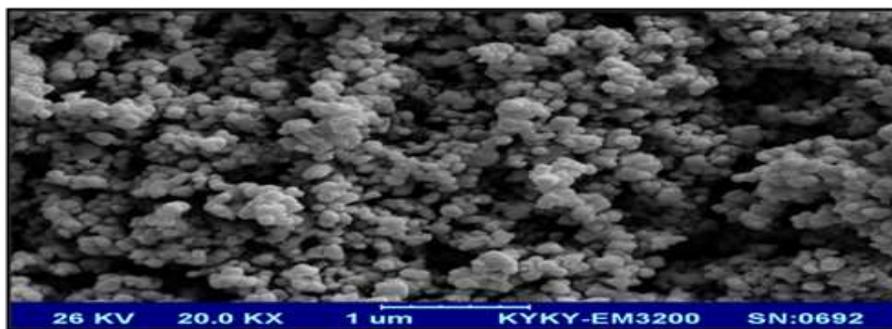
- 1) The peaks at  $2\theta = 31.7^\circ$  and  $36.2^\circ$  are related to the ZnO that has the hexagonal crystal lattice in two synthesized nanopigments.
- 2) The peak illustrated at  $2\theta = 65.2^\circ$  shows the cobalt oxide with cubic crystal lattice in two samples.
- 3) The peak at  $2\theta = 89.23^\circ$  confirms the presence of calcium oxide with cubic crystal lattice in two samples of nanopigments.

The results depict the successful formation of the desired phases. The average sizes of the synthesized nanopigments were reported to be about 31.7 and 19 nm using the Scherrer equation for two proportions of 3:1 and 1:3, respectively. The calculations for determining the average size of particles was carried out using [Formula 1].

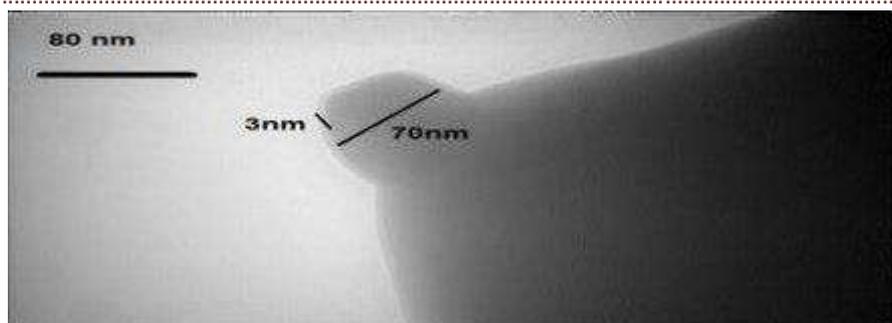
Formula 1:

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

where D is the size of crystal beads,  $\lambda$  is the wavelength of X-ray,  $\beta$  is the peak width in the half of maximum intensity (radian), and  $\theta$  is the diffraction angle. [Fig. 3] and [Fig. 4] show the SEM and TEM images of the synthesized nanopigments with the proportion of 1:3. The results obtained from SEM, illustrated in [Fig. 3], confirms the presence of non-uniform spherical particles. Also, the size of particles has been reported within the range of 47–100 nm. [Fig. 4] depicts the transmission electron microscopy images that confirm the presence of a core with a thickness of 70 nm which is covered with a thin and uniform shell with a thickness of 3 nm. According to these images, the particle size has been reported to be lower than 100 nm.

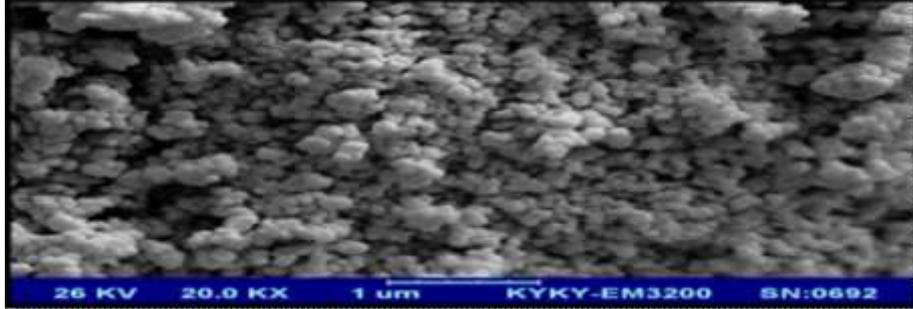


**Fig. 3:** The SEM image of the 1CoO.3CaO/ZnO nanopigment with 20,000 times magnification.

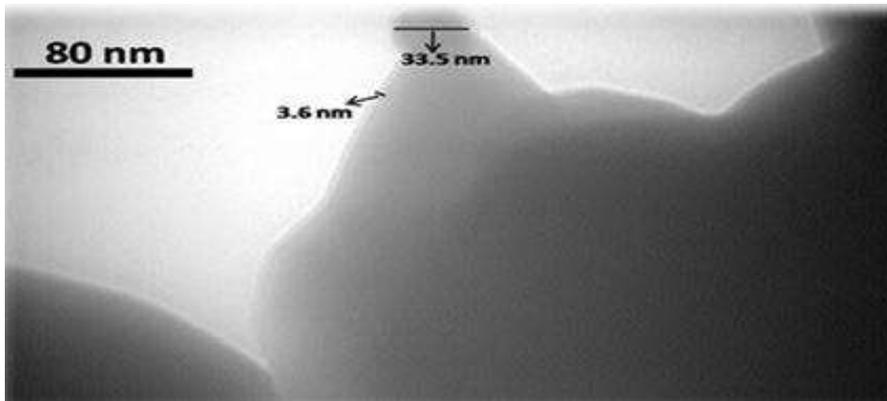


**Fig. 4:** The TEM image of the 1CoO.3CaO/ZnO nanopigment.

The results obtained from TEM and SEM analyses for the nanopigment with the proportion of 3:1 have been illustrated in [Fig. 5] and [Fig. 6]. The results of the TEM analysis, shown in [Fig. 5], depict the non-uniform spherical shape of particles. The size of particles has been reported to be within a range of 41.3–98.9 nm. As shown in [Fig. 6], the results of TEM confirm the presence of a core with a thickness of 33.5 nm which was covered by a thin and uniform shell with a thickness of 3.6 nm. It should be mentioned that the proportions of the core and shell in the synthesis of the nanopigments are about 80% and 20%, respectively. The major part of the core is ZnO and the remaining 20% is related to the different oxides of cobalt and calcium as the shell.



**Fig.5:** The SEM image of the 3CoO.1CaO/ZnO synthesized nanopigment with 20,000 times magnification.



**Fig.6:** TEM image of the 3CoO.1CaO/ZnO nanopigment with 125,000 times magnification.

The results obtained from the rheological or cooking properties of rubber compounds containing new nanopigments, compared to the reference sample, have been presented in [Table 2]. As can be seen, the amount of the maximum moment (MH) increases by adding nanopigments based on elastomer compounds compared to the reference sample. The reason for this increase can be attributed to the presence of nanopigments and strong interactions with the polymer matrix. Owing to an increase in the effective contact surface of nanopigments and strong bonds (Van der Waals forces or chemical bonds) connecting the polymer chains to the surfaces of nanopigments, the cross-links increase, resulting in a decrease of polymer chains in the rubber compounds and an increase in the maximum moment [4, 6]. The minimum moment (ML), which is defined as a level of hardness in the vulcanized compound, shows a constant trend at the beginning of the cooking process. The  $\Delta M$  parameter is the density of cross-links; it is obtained from the difference between the maximum and minimum moments. The results illustrate the increase in the  $\Delta M$  parameter. The changes of the cooking moment by loading nanopigments can be used to determine the interactions or the level of boosting between the nanopigment-polymer matrix [3]. This factor is named as the reinforcement factor or  $\alpha_f$ , which is calculated using [Formula 2].

Formula.2:

$$\frac{D_{max} - D_{min}}{D_{max}^o - D_{min}^o} - 1 = \alpha_f \frac{m_f}{m_p}$$

where  $D_{max} - D_{min}$  is the maximum changes of moment during the cooking process for the rubber loaded by nanopigments,  $D_{max}^o - D_{min}^o$  is the maximum changes of moment during the cooking process for the raw rubber,  $\alpha_f$  is the reinforcement coefficient,  $m_f$  is the mass of nanopigment,  $m_p$  is the mass of elastomer base used [1]. As presented in [Table 2], the amount of reinforcement increases by loading nanopigments compared to the reference sample. This increase in the sample with a proportion of 3:1 is more than the increase in the sample with a proportion of 1:3. This increase can be due to the strong interfacial

interaction of the nanopigment-polymer matrix. These positive changes show the boosting effects of the new core-shell nanopigments [1]. Three other significant parameters are scorch time ( $T_{s2}$ ), the optimal time for cooking or  $T_{c90}$  (the time needed to reach the 90% of final moment), and the cooking rate index (CRI). Loading the new core-shell nanopigments reduces the optimal time for cooking because of the effects of nanopigments on the decreasing time required for the sulfuring process in the cooking. Also, a uniform distribution of nanopigments into the nitrile elastomer matrix not only reduces this parameter, but also improves the process of producing and saving energy [6]. On the other hand, the effects of chemical active sites and surface properties of the new core-shell nanopigments cause an effective interaction between the nanopigments and polymer chains as well as increase the formation of cross-links in the polymer. As a result, the vulcanization process takes place quickly to decrease the optimal time for cooking [3, 6]. Also, the cooking rate index of the rubber compound loaded by the 1CoO.3CaO/ZnO nanopigment increases, and the 3CoO.1CaO/ZnO nanopigment shows the similar behavior with the reference sample. The scorch time is decreased by loading the core-shell nanopigments.

**Table2:** The results obtained from the rheological properties (cooking)

Core-Shell pigments 15 phr	Sample number		$M_L$	$M_H$	$T_{c90}$	$T_{s2}$	CRI	$f_a$	$\Delta M$
			dN.m	dN.m	min:sec	min:sec	min <sup>-1</sup>		( $M_H-M_L$ )
	Z <sub>b</sub>	Without Pigments	0.552	6.208	14:55	6:04	11.303	-----	5.656
	Z <sub>1:3</sub>	1CoO.3CaO/ZnO	0.552	6.484	13:16	5:48	13.387	0.32	5.932
	Z <sub>3:1</sub>	3CoO.1CaO/ZnO	0.552	7.173	13:22	5:34	11.303	1.13	6.621

Z<sub>b</sub>: The reference sample without the nanopigments.  
 Z<sub>1:3</sub>: The sample containing 15 phr of 1CoO.3CaO/ZnO nanopigment.  
 Z<sub>3:1</sub>: The sample containing 15 phr of 3CoO.1CaO/ZnO.

Another test was the tensile test carried out on the rubber compounds loaded by the new core-shell nanopigments. The results obtained from the tensile test have been depicted in [Table 3].

**Table 3:** The trend of changes in the physicomechanical properties of the rubber compounds containing nanopigments and the reference sample

Sample number		Stress N/mm <sup>2</sup>	Elongation mm	Modulus 100% N/mm <sup>2</sup>	Modulus300% N/mm <sup>2</sup>
Z <sub>b</sub>	Without Pigments	2.16	236.44	1.04	1.84
Z <sub>1:3</sub>	1CoO.3CaO/ZnO	2.10	210.04	1.22	2.01
Z <sub>3:1</sub>	3CoO.1CaO/ZnO	2.20	227.03	1.20	2.00

As can be seen, the improvement in physicomechanical properties is related to loading the nanopigments in such a way that this increase shows a good interaction between nanopigments and polymer. A slight increase of the tensile strength in the rubber compound containing 3CoO.1CaO/ZnO is due to the improvement of interfacial bonds between the nanopigments-polymer matrix because a strong interaction can lead to the increase and transfer of resulting tensions from the polymer matrix to the core-shell nanopigment distributed into the rubber compound [3, 6]. More improvement in the tensile modulus about 300%(Tensile stress at 300% elongation. also known as "300% Moduluse") and 100%(Tensile stress at 100% elongation. also known as "100% Moduluse") compared to the reference sample confirms a uniform distribution of nanopigments into the polymer matrix along with the interaction of the nanopigment-polymer matrix. This raises the effects of tensions transformed from the polymer matrix into the nanopigments distributed in the rubber compound [3, 6]. Another significant parameter is the reduction of the increased length in the breaking point-this decreases in two rubber compounds containing the new nanopigments compared to the reference sample. This can be attributed to the increase of the boosting power by the core-shell nanopigments and the polymer chains being harder. Hence, the flexibility of vulcanized rubber gets decreased [3].

### CONCLUSION

In this research, the synthesis of 1CoO.3CaO/ZnO and 3CoO.1CaO/ZnO core-shell nanopigments with two different proportions of the shell and their effects on the cooking and physicomechanical properties of rubber compounds based on the acrylonitrile butadiene elastomer were investigated. Also, the XRD analysis showed the formation of the desired phases. The images obtained from SEM and TEM analyses confirmed the spherical shape of particles, the size of nanoparticles within the range of lower than 100 nm, and the formation of a thin shell layer on ZnO, respectively. Also, the results related to the rubber compounds containing nanopigments with the NBR base illustrated that the presence of new core-shell nanopigments can improve the cooking properties, especially the optimal time for cooking. The improvement of this parameter depends on different factors such as the size of particles, the increase of effective surfaces in new nanopigments, and the presence of chemical active sites. These factors can make strong and effective interactions between the nanopigments and the polymer matrix. Also, formation of strong bonds (Van der Waals forces or chemical bonds) increases the cross-links that improve the

cooking properties. It should be mentioned that decreasing the cooking time is vitally important to save energy in the polymer industry. Another factor was the boosting power of rubber compounds containing the nanopigments compared to the reference sample. The increase in the boosting power in rubber compounds based on the nitrile elastomer confirms the effective role of core-shell particles. The results achieved from the tensile test show the improvement of the desired properties in the rubber compounds based on the NBR elastomer. This can be attributed to the improvement of interfacial bonds between the nanopigments and the polymer matrix. Also, because of the uniform distribution of new nanopigments and increases in the contact surface of nanoscale, strong interactions take place between the polymer matrix and the nanopigments, resulting in the increase and transfer of tensile forces from the polymer matrix to the core-shell nanopigments. The new inorganic core-shell nanopigments can be a suitable alternative for reducing the usage of organic pigments that pollute the environment. According to the optical and thermal stability as well as the environment-friendly properties, the inorganic core-shell pigments can be a good alternative to organic pigments. The new synthesized green nanopigments have unique properties that can compete with organic pigments.

#### CONFLICT OF INTEREST

There is no conflict of interest.

#### ACKNOWLEDGEMENTS

None

#### FINANCIAL DISCLOSURE

None

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