



## Original Research Article

# Ternary NR/BR/SBR Rubber Blend in the Presence of Nano Additives

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## KEYWORDS

Nano clay

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Natural Rubber (NR)

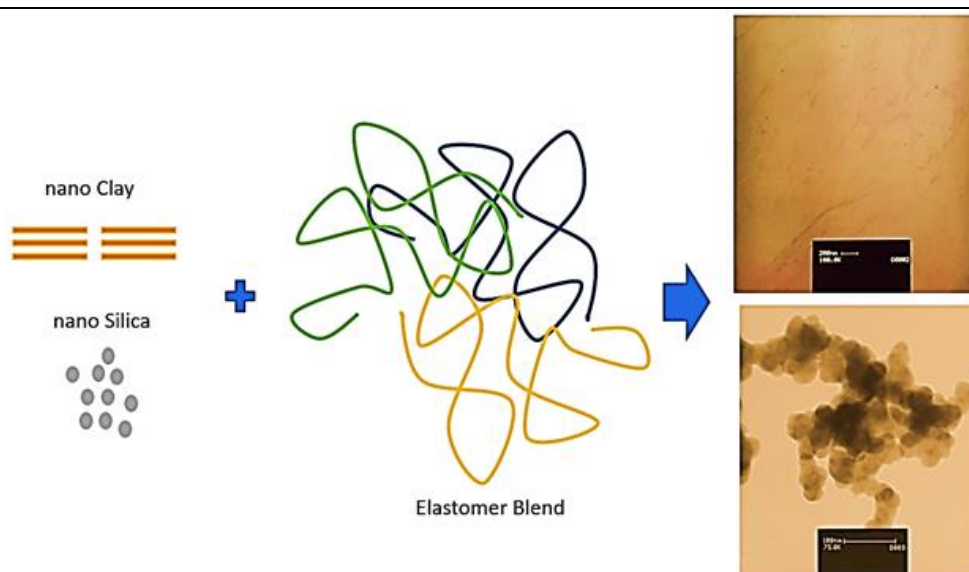
Butadiene Rubber (BR)

Styrene Butadiene Rubber (SBR)

## ABSTRACT

A ternary nanocomposite containing natural rubber, butadiene rubber, and styrene-butadiene rubber (NR/BR/SBR blend) was prepared in 25/25/50 (phr), on which the effect of adding carbon black, nano clay (C15A), and nano-silica was examined. Rheometric, tensile, and hardness measurement tests were performed on the prepared samples. The nano silica-containing sample showed an inhibitory effect in curing, while the modified nano clay-containing sample showed an accelerating effect on the curing process. The results revealed that the presence of nano-silica caused higher elongation at break. TEM analysis was performed from cross-linked samples to ensure the exfoliation of nano additives in the matrix. The results confirmed the suitable distribution and dispersion of the nanoparticles in the composite samples.

## GRAPHICAL ABSTRACT



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## Introduction

Blending elastomers is the most effective method for developing new compounds [1, 2]. Natural rubber, styrene-butadiene rubber, and butadiene rubber are commonly used elastomers in the rubber industry [3]. Natural rubber is widely used in the rubber industry because of its high elasticity, oil resistance, impermeability against air and ozone resistance, low set, and high aging resistance [4]. In a brittle mixture, high corrosion resistance with special conditions is required. Blending butadiene, which has low resistance to road bumps and spalling, with NR and SBR well covers this need [5]. SBR is used in the tire, cable, and wire industry because of elongation at break; however, it has low elasticity modulus and durability [6, 7].

The main aim of adding fillers to elastomers is to enhance properties and lower production costs [8]. The reinforcing fillers added to the rubber compound, through enhancing the modulus, offer high mechanical properties and high abrasion resistance [9]. The suitable dispersion of nanosized materials induces a strong interfacial attraction with the polymer matrix [10]. Thus, adding less than 5 wt% of these materials cause improvement in properties such as thermal stability, mechanical, dynamic and mechanical, impermeability, and optical properties in polymer matrixes [11-13].

Nano clay is a planar filler with a very high specific surface area (at about 750 m<sup>2</sup>/g) belonging to the silicate family with planes with about 1 nm thickness [14]. The efficiency of nanoclay in improving the nanocomposite properties depends on the nature of nano clay, its dispersion, rubber compatibility, and process conditions. Exfoliation of clay at less than 5% by weight results in remarkable improvement in nanocomposite properties [15]. Clay nanosheets are widely used as reinforcement material because of their low-cost and easy accessibility [16]. Nanomaterials are added to the elastomer

via solution intercalation, melt blending, and in-situ polymerization methods [17]. Sparse studies have been performed on NR/BR/SBR triple compounds with nanomaterials [15].

Several studies have been performed on developing reinforcer materials to replace carbon black in rubber compounds [18]. It is believed that improvement of mechanical properties can be realized by adding nanosilica particles because of hydroxyl groups on their surface (isolated silanol groups with hydrogen bonds) [12]. These groups enhance interphase interaction and tend toward clustered aggregation. Thus, they reduce the filler-rubber interaction in most rubber matrixes [12]. Meanwhile, silica with silane coupling agents instead of carbon black develops advantages such as improving rolling resistance, tear strength, and gripping under humidity conditions in rubber [12].

In this research study, a ternary compound containing natural rubber, butadiene rubber, and styrene-butadiene rubber, named NR/BR/SBR composite, was prepared by adding nano-silica and nano clay filler. The effect of the addition of nanoparticles into the composite compared with the one with no reinforcement nanoparticles was evaluated using rheometric, tensile, hardness measurement, and transmission electron microscopy (TEM) tests.

## Experimental

### Materials

Natural rubber (NR) with SMR20 grade with Mooney viscosity of Ml (1+4) 100 °C=70 M and density of 0.916 g/cm<sup>3</sup> was purchased from Malaysia, butadiene rubber (BR) with Mooney viscosity of Ml (1+4) 100 °C=43 M and density of 0.990 g/cm<sup>3</sup> from Arak Petrochemical Complex, and styrene-butadiene rubber (SBR) with Mooney viscosity of Ml (1+4) 100 °C=49 M and density of 0.942 g/cm<sup>3</sup> from Bandar Imam Petrochemical complex. Modified clay, i.e.,

Cloisite 15 A (C15A), with a cation exchange capacity of 125  $m_{\text{equiv}}/100 \text{ g}$  was purchased from Southern company of USA. Silica nanoparticles with a mean particle size of about 20 nm and purity of above 99%, and a specific surface area of 440  $m^2/g$  were purchased from Ekp Co, France. Zinc oxide (ZnO) was procured from Pars Oxide Parto Co., stearic acid with 401860 grade from Indonesia, carbon black (CB) with N330 grade and specific surface area of 78  $m^2/g$  from Carbon Simorgh Co., aromatic-based process oil (Behran Tyre 290) with viscosity and density factor ratio of 0.96 (VGC) from Behran Co., 3-dimethyl butyl-n-phenyl paraphenyline diamine (6PPD) with purity above 95% and N-cyclohexyl-2-benzothiazide sulfonamide (CBS) with purity above 96% from China, tetramethyl thiuram disulfide (TMTD) from Baer Belgium, and sulfur from Parto Gugerd Asia Co.. All materials were used without purification and as received.

#### Synthesis method

In a typical synthesis, initially, NR underwent a mastication process for 5 min. Next, NR (25 phr) alongside BR (25 phr) and SBR (50 phr) were

**Table 1.** The composition of the materials in parts per hundred of rubber (phr) utilized for preparing the compounds

	N R	B R	SB R	Zn O	Steari c acid	C15 A	Silic a	C B	Aromat ic Oil	6PP D	Paraffi n wax	CB S	TMT D	Sulph ur
Unfilled	25	25	50	5	2	0	0	0	5	1	1	1	0.1	1.5
CB	25	25	50	5	2	0	0	60	5	1	1	1	0.1	1.5
Silica	25	25	50	5	2	0	40	0	5	1	1	1	0.1	1.5
C15A	25	25	50	5	2	5	0	0	5	1	1	1	0.1	1.5

#### Characterization techniques

Rheometer ODR 2000 (Avaye Danesh Afarin Co.) was used to obtain optimal curing conditions at 160 °C and under ASTM D2084 standard for each blend. The prepared blends were cured at 170 °C and pressure of 150 bar. Thermogravimetric analysis, TGA/DTA (Model TGA PT 1000, Linseis Co., Germany), under nitrogen atmosphere was used from room

temperature up to 600 °C at a 20 °C/min rate. Santam tensile device (STM-400, Iran) was also used for measuring the tensile strength of the samples prepared under the ASTM-D624 standard. Further, using the ASTM-D2240 standard, the hardness of the cured samples was measured. A transmission electron microscopy (Philips EM-2085) with a voltage of 100 kV was employed to evaluate the dispersion of

nanoparticles across the matrix of the cured blends. Before the study, the samples were cured in epoxy resin and cut into layers with 60-100 nm thickness using cryo-ultramicrotomy.

## Results and Discussion

To evaluate the effect of the addition of three fillers, rheological studies were performed at 160°C. The results are provided in Table 2.

The strong interaction between silica particles arises from surface functional groups, such as siloxanes. These intermolecular forces cause enhanced minimum momentum ( $M_{min}$ ), representing initial viscosity and matrix and filler interactions. Meanwhile, acidic silanol groups (Si-OH) on the silica surface [19, 20] delays

vulcanization. It has been reported that vulcanization of NR in the presence of silica does not occur without increasing the accelerator content [4]. Also, silica particles further intensify the deactivation of vulcanization of the elastomer, which may be attributed to the absorption of polar molecules of curing agents on silica nanoparticles. In the presence of SBR, phenyl groups enter the structure, with these groups leading to the development of a strong hydrogen bond with silica. Thus, the maximum momentum, which indicates the size of the shear modulus of vulcanized rubber in the NR/BR/SBR triple system, grows with increasing the SiO<sub>2</sub> content. Note that the curing process of SBR is slower than that of NR and BR [12].

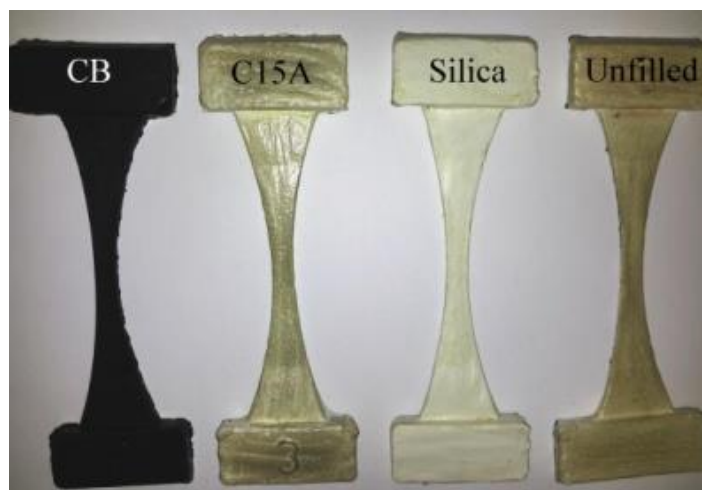
**Table 2.** The curing characteristics of the NR/BR/SBR triple blend with three types of filler

NR/BR/SBR- Filler content	Optimal curing time	Scorch time	$M_{max}$	$M_{min}$
	$t_{90}$ (s)	$t_5$ (s)	(dNm)	(dNm)
25/25/50	1.01	0.62	5.23	0.51
25/25/50-60 CB	0.72	0.35	15.71	2.12
25/25/50-40Silica	1.35	0.46	8.24	1.49
25/25/50-5C15A	0.62	0.21	6.25	1.02

Upon addition of clay to the triple mixture, the optimal curing time and scorch time diminish, causing an enhanced curing rate and maximum momentum of the cured sample. Since vulcanization is intensified at higher pH, thus researchers believe that the amine functional groups modified in clay are used as cationic exchange agents, causing activation of sulfur and acceleration of the curing process. The probability of forming a complex between Zn and sulfur and ammonium present in the interlayer space of the modified clay sheets leads to intensified vulcanization. The addition of

nanoclay to the matrix, due to its high surface area and development of high interaction with polymer chains, establishes high resistance against the blend's flowability and inhibits its molecular motion. This leads to an increase in both minimum and maximum momentum. Meanwhile, the elevation of the density of -links in nanoclay also contributes to this enhancement [7].

To evaluate the effect of filler type on the properties of the final product, standard sheets were fabricated from the prepared samples and punched, as demonstrated in Figure 1.

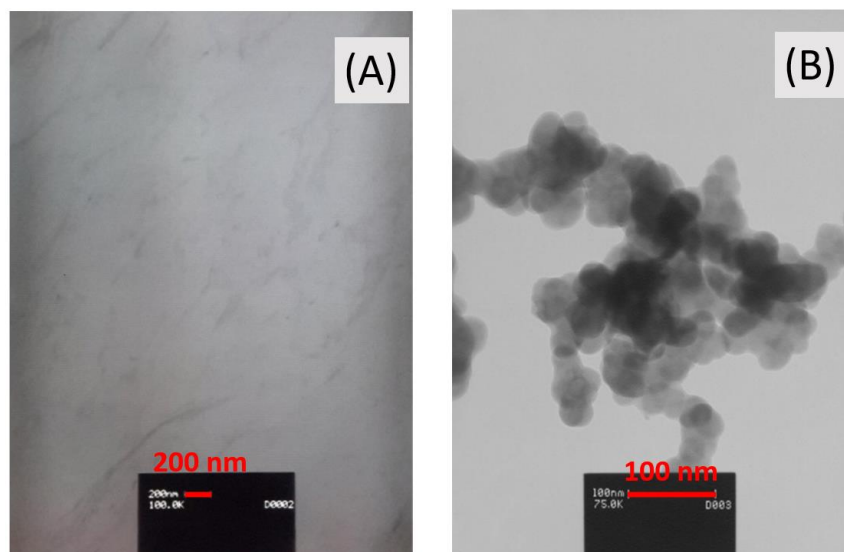


**Figure 1.** Image of the prepared and punched samples

The results of tensile and hardness measurement tests are presented in **Table 3**. The presence of 60 phr CB in the blend resulted in a considerable increase in the tensile strength of the cured sample by around 15.3 MPa, which is due to numerous functional and polar groups across the N330 CB surface. Further, 40 phr silica also conferred 5.5 MPa increase of strength to the triple blend. A simple comparison shows that the addition of clay nanoparticles caused more significant enhancement of tensile strength and elongation at break than the others, regardless of the different content of fillers. This improvement of mechanical properties in response to adding nanoclay depends on the extent of intercalation or layering of clay sheets and constricted movement of the polymer chain due to the presence of rigid clay sheets in the matrix. The high L/D ratio of clay nanosheets is responsible for the high resistance of polymer chains in clay containing nanocomposite sample against crazing compared to the one containing spherical particles. It has also been reported that the

orientation of nanosheets in response to the exerted stress would cause enhanced tensile strength of the clay containing nanocomposite sample [21]. The development of physical attachments also causes improved mechanical properties of the nanocomposite. Research has shown that in samples with more than 5 wt% nano clay, due to the development of stress concentrating points, the mechanical properties of the final product diminish [21]. An increase in tensile strength upon adding nano-silica suggests the reinforcing effect of this filler. Very strong interactions between these nanoparticles and polymer chains could cause this reinforcement.

Figure 2 (A, B) displays the TEM images of two samples of NR/BR/SBR triple blend reinforced with nanoparticles. Figure 2A clearly shows the layering of clay nanosheets, and Figure 2B shows suitable dispersion of silica nanoparticles. As shown in Figure 2, layering and suitable dispersion of nano additives in the **NR/BR/SBR composite can** confirm the improvement of properties in the prepared nanocomposites.



**Figure 2.** TEM images of NR/BR/SBR triple samples with nanoclay (a) and nano-silica (b) fillers

**Table 3.** Results of tensile analysis on the prepared samples

NR/BR/SBR- Filler content	Hardness (°Sh)	Elongation at break (%)	Tensile strength (Mpa)
25/25/50	35	197	1.6
25/25/50-60 CB	39	425	16.9
25/25/50-40 Silica	44	642	7.1
25/25/50-5 C15A	40	352	2.97

## Conclusion


A ternary NR/BR/SBR nanocomposite via the addition of different fillers, including silica nanoparticles, nano clay, and carbon black, was synthesized and characterized to evaluate the mechanical and morphology properties. The addition of nano-silica to the raw blend caused increased curing time, while the presence of nanoclay resulted in an accelerated curing process. The results also revealed that the addition of nanoparticles at very trace amounts, especially nanoclay caused improved physical and mechanical properties. This study revealed that it is possible to reduce the amount of carbon black, as the main filler and reinforcer, in rubber compounds by selecting the suitable nanoadditive and tuning the nanocomposite formulation.

## Disclosure statement

No potential conflict of interest was reported by the authors.

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