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Research Article

Effect of Nanoclay Modification on Properties of Natural Rubber Nanocomposites Using Zinc Compound

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Abstract: This study investigates the effect of nanoclay modification on the properties of natural rubber (NR) nanocomposites using zinc stearate (ZS) and di(hydrogenated tallow) dimethylammonium chloride (DHDT). The aim is to enhance the compatibility of modified nanoclay (NC) and NR molecules for determining cure characteristics, mechanical properties, and morphologies. The effect of unmodified and modified NC as the secondary filler was studied using the 10 phr NC regarding the received properties of the silica-based composites. Results indicated that the NR composites with modified NC exhibited a significant improvement of 32.06% estimated crosslink density, 16.6% tensile strength, 30.1% Payne effect together with the production time of 3.9 min relative to the composites with unmodified NC. This related to the dispersion and distribution degree of the NC and it suggests that the modification of nanoclay with ZS and DHDT can positively impact to the NR nanocomposites, enhancing their mechanical performance and processing characteristics.

Keywords: Modified nanoclay, Natural rubber, Nanocomposites

1. Introduction

Natural rubber (NR) nanocomposites have emerged as a promising class of materials due to their ability to significantly enhance a wide range of properties essential for various applications. NR, derived from the latex of certain plants, possesses inherent elasticity and resilience, making it invaluable in industries such as automotive, medical, and industrial sectors. However, to further extend its utility and improve its performance characteristics, researchers have turned to nanotechnology. Nanocomposites are materials composed of nanoscale fillers, such as nanoclays (NC), carbon nanotubes (CNT), graphene (GP), or silica (SiO_2), dispersed within a polymer matrix (i.e., NR) to enhance properties, especially the mechanical properties, electrical conductivity, dielectric constant, and thermal stability [1-4]. Among the various nanofillers, NC is particularly noteworthy due to their natural abundance and low cost. Clays exhibit a unique flake-like structure that improves plasticity and bonding strength, with montmorillonite clay being particularly notable due to its high cation-exchange capacity. In addition, particle size varies between different clay types, with montmorillonite capable of breaking into smaller particles, thus providing a larger surface area for interaction. The expanding lattice of montmorillonite allows water molecules to enter between the layers, resulting in swelling and increased plasticity. These distinctive features profoundly affect the mechanical and chemical behaviors of clays across

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diverse applications [5]. It was also reported that incorporating NC into rubber can substantially enhance its mechanical and chemical properties and improve its abrasion and swelling resistance [6-9]. Therefore, the intercalation or exfoliation of NC layers is crucial for the performance of rubber composites. However, the direct use of unmodified clays in NR often leads to poor dispersion and weak interfacial interactions due to the inherent low polarity of NR and smooth surfaces of NC, which causes poor bound rubber absorption. This results in nanocomposites with suboptimal properties, limiting their effectiveness in practical applications. To address these challenges, it is crucial to modify clays to improve the dispersion of NC within the rubber matrix and reduce their agglomeration. This modification technique often involves surface alteration through ion exchange reactions using quaternary ammonium salts or surface modifiers that replace sodium ions (Na^+), thereby increasing the distance between NC layers. This allows for better intercalation of rubber between the clay layers, leading to improved properties of the prepared composite. Sedničková et al. [10] investigated the surface modification of montmorillonite clay (MMT) using octadecyl trimethylammonium (ODTMA) and oleyl trimethylammonium (OLEYL). They found that the cure characteristics and tensile properties improved after adding the modifying agent, due to the dispersion and distribution of MMT within the NR matrix. Similarly, Lolage et al. [11] modified the organoclay (OC) with octadecyl amine and aminopropyltriethoxysilane (APTES) and observed a reduction in scorch time, while the ductility, wet traction, and rolling resistance of styrene-butadiene rubber (SBR) and butadiene rubber (BR) blends improved with the use of 5 phr of modified OC. These findings highlight the advantages of surfactant-modified clays in optimizing the performance of rubber composites. Thus, the challenges and promising aspects of using clay in rubber lie in the chemicals and modification procedures of the modifying agent, which must be carefully tailored to achieve optimal production and composite properties.

The present work presents the results of NR composites filled with unmodified and modified clays, incorporating zinc stearate (ZS)-based di(hydrogenated tallow) dimethylammonium chloride (DHDT), which is used to replace the sodium ion (Na^+) among the clay interlayers. This modification expands the clay layers, improving the dispersibility of the clay within silica-filled NR composites. This enhanced compatibility with hydrophobic NR could be further considered a modified clay suitable for optimizing production time, specifically in terms of cure characteristics. The mechanical properties, such as tensile strength, elongation at break, modulus, and the Payne effect—which directly relates to the degree of filler agglomeration, including silica, clay, and silica/clay agglomeration within the NR matrix—are also improved.

2. Methodology

2.1 Materials

Natural rubber (NR), 1,2-Dihydro-2,2,4-trimethylquinoline (TMQ), and N-Cyclohexylbenzothiazol-2-sulphenamide (CBS) were purchased from Bossoftical Public Company Limited (Songkhla, Thailand). ULTRASIL VN23 Silica (SiO_2) and bis(3-(triethoxysilyl)-propyl) tetrasulfide (TESPT) were obtained from Evonik Industries AG (Wesseling, Germany). Bentonite Clay was purchased from Siam Eastern Industrial Park Company Limited (Rayong, Thailand). Zinc-based organoclay modified with zinc stearate (ZS) and di(hydrogenated tallow) dimethylammonium chloride (DHDT) using the technique of cation exchange involves replacing Na^+ ions in the clay with ions from the modifiers, zinc oxide (ZnO) and sulfur were provided by Global Chemical Company Limited (Samut Prakan, Thailand). Stearic acid was purchased from Imperial Chemical Company Limited (Pathum Thani, Thailand). Diphenylguanidine (DPG) was purchased Shenyang Sunnyjoint chemicals Company Limited (Liaoning, China).

2.2 Preparation of the NR composites

The preparation process for NR composites filled with unmodified and modified NC is conducted in two steps using an internal mixer. In the first step, the masterbatch is mixed at an initial temperature of 60 °C. The dumping temperature is set at 130 °C with a rotor speed of 60 rpm. Initially, NR is masticated, followed by adding various chemicals listed in Table 1, excluding accelerators and sulfur. This mixing process lasts for 15 min. Moving to the second step, the rubber compound is mixed at 70 °C with a rotor speed of 30 rpm. The rubber masterbatch is mixed with accelerators and sulfur for 3 minutes. Subsequently, the compound is transferred to a two-roll mill to enhance filler dispersion throughout the NR matrix and to sheet the mixture. After completion, allow the compound to cool to room temperature before proceeding to rheometer testing. The quantities of TESPD and DPG were adjusted based on the silica contents, following Equations (1) and (2) [12] shown below:

$$\text{TESPD (phr)} = 0.00053 \times Q \times A \tag{1}$$

$$\text{DPG (phr)} = 0.00012 \times Q \times A \tag{2}$$

where Q indicates the quantity of silica (phr). A signifies the specific surface area of the silica determined using cetyl-trimethyl-ammonium bromide (CTAB), which is 171 m^2/g.

Table 1 Formulation of the NR/SiO_2 composites filled with unmodified and modified NC

Ingredients	**Content (phr*)**
Natural rubber (NR)	100
Silica	45
Unmodified and modified NC	10
TESPT	4.1
ZnO	3
Stearic acid	1
TMQ	1
DPG	0.9
CBS	1.5

*Parts per hundred of rubber

2.3 Characterizations

Particle size

The particle size distribution (PSD) of both unmodified and modified NC powder was measured using a Partica LA-960 analyzer (HORIBA Limited, Kyoto, Japan).

X-ray diffraction

X-ray diffraction (XRD) analysis was conducted on dried powder samples using a Smart Lab SE instrument (Rigaku Corporation, Tokyo, Japan) equipped with Cu Kα radiation (λ=0.1542 nm) to identify crystalline phases. Data collection spanned the 2θ range of 5 to 30 degrees. The d001 spacing was determined using Bragg's equation: nλ=2dsinθ.

Curing characteristics

Curing characteristics, including parameters such as initial cure time (t_{s2}), optimum cure time (t_{90}), and peak torque values (M_H, M_L), were analyzed using the Rubber Process Analyzer RPA2000 (Alpha Technologies, Ohio, USA) at a temperature of 150 °C for 30 minutes.

Scanning electron microscope (SEM)

The fractured surfaces were coated with a thin layer of gold before analysis. Subsequently, observations were conducted using a Phenom ProX scanning electron microscope (SEM) (Thermo Fisher Scientific, Eindhoven, Netherlands).

Tensile properties

The tensile properties were evaluated at room temperature using a universal testing machine (Zwick Z 1545, Zwick GmbH and Co. KG, Ulm, Germany). The testing procedure followed ISO 037 (Type 2) standards, employing a 500 N load cell and a crosshead speed of 200 mm/min. Each sample was tested using five dumbbell specimens, and the results were averaged. The parameters assessed included tensile strength, elongation at break, and moduli at 100% and 300% elongations.

Payne effect

The Payne effect was investigated by measuring the storage shear moduli (G') of rubber compounds containing curatives using a Rubber Process Analyzer RPA 2000 (Alpha Technologies) at 100 °C and a frequency of 0.5 Hz, with strains ranging from 0.56% to 100%. The Payne effect was characterized as the difference in storage shear moduli between low strain (0.56%) and high strain (100%).

3. Results and discussion

Particle size analysis and X-ray diffraction (XRD)

The particle sizes of unmodified and modified NC are shown in Table 2. It was found that the NC particle sizes increased after modification with ZS-DHDT, due to structural expansion [13]. This suggests that ZS-DHDT interacts with the NC surface, promoting ion exchange that increases interlayer spacing and hydrophobic interactions. These modifications cause the NC particles to break apart from aggregates, resulting in larger, more hydrophobic particles.

Based on Figure 1, the XDR analysis of unmodified and modified NC with ZS-DHDT indicated that the maximum reflection occurs at a 2θ angle of approximately 6.2 degrees. This reflection angle corresponds to a d-spacing of 1.42 nm for the modified NC. However, according to the results of XRD stated elsewhere [14-16], the unmodified NC showed maximum reflection angles of approximately 7.0-8.0 degrees, with d-spacings of about 1.11-0.98 nm, which are lower than those observed in the modified NC case. This clarifies well the expandability of the modified NC reading to the shift in the reflection angle and the d-spacing, indicating changes in the internal structure of NC. This change signifies successfully incorporating the modifying substances into the NC structure, thereby altering its physical properties.

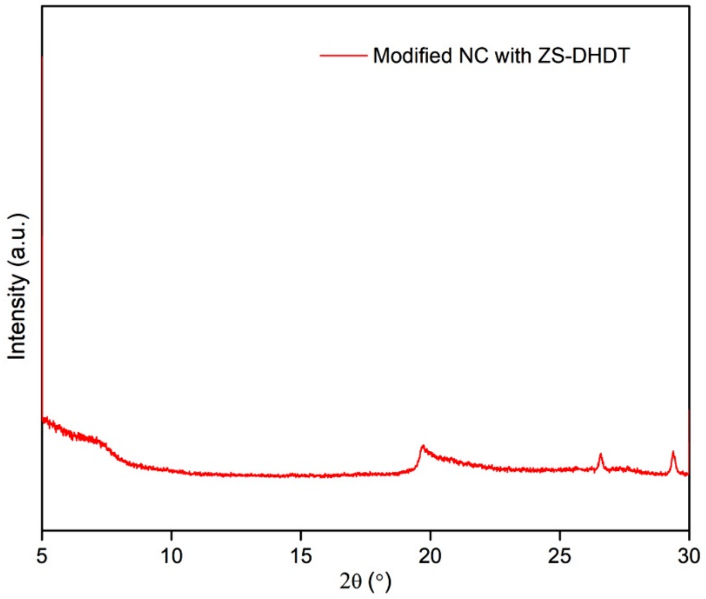

Figure 1 XRD data of modified NC with ZS-DHDT together with detail from the testing.

Table 2 Particle size of the unmodified and modified NC with ZS-DHDT

Name	Particle size (μm)
Bentonite clay	<10
Organoclay zinc	15.32

Further supporting this finding, studies by Singla et al. [17] have shown similar shifts and increases in d-spacing when different surfactants were used for organoclay modification. These alterations often lead to enhanced properties, such as improved compatibility with rubber, which can benefit various applications. Understanding the intercalation mechanism not only reinforces these findings but also suggests potential pathways for optimizing the modification process in future research.

Cure characteristics

Figure 2 shows the cure curves for the NR/SiO_2 composites filled with unmodified and modified NC. Both composites exhibit a gradual decrease in torque after reaching the peak, which suggests a slight reversion or degradation of the crosslinked network over time. This phenomenon can occur due to over-curing or breaking some crosslinks at elevated temperatures. The NR/SiO_2 composite filled with modified NC maintains a higher torque over time than the unmodified NC composite, indicating better thermal stability or resistance to reversion. Additionally, Table 3 shows that the cure characteristics, scorch time (T_{s2}), and cure time (T_{90}) of the modified NC composite are shorter compared to the composite filled with unmodified NC. This is because, in NR composites with modified NC, the amine molecules from the ammonium groups of the modifier agent in the clay actively participate in the vulcanization reaction. These molecules can act as additional accelerators, speeding up the formation of crosslinks [18]. The torque difference (M_H-M_L) is recognized as the estimated crosslink density within the composites [19,20]. It was found that the use of the modified NC showed an increase in M_H-M_L values. This is because organoclay zinc typically provides better dispersion and interaction with the NR matrix than the unmodified NC.

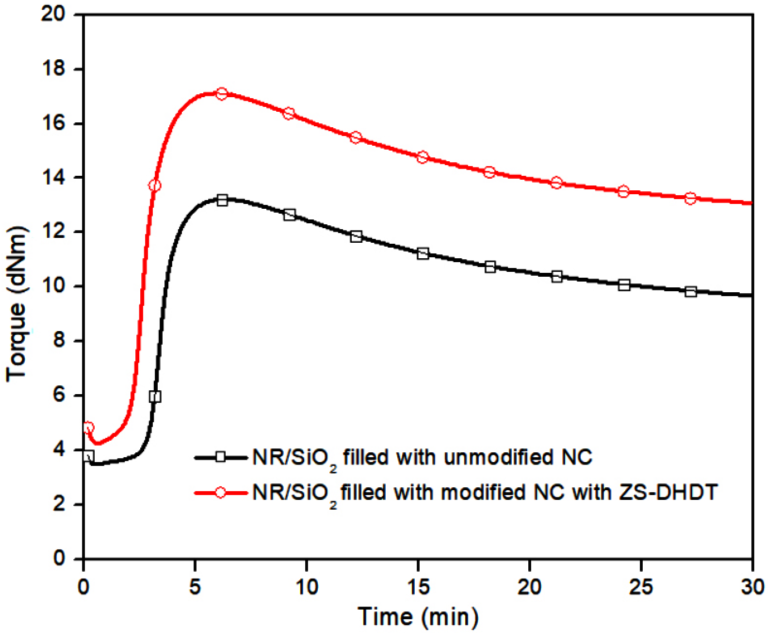

Figure 2 Cure curves of the NR/SiO_2 composites filled with unmodified and modified NC with ZS-DHDT.

Table 3 Cure characteristics of the NR/SiO_2 composites filled with unmodified and modified NC with ZS-DHDT

Properties	NR/SiO_2 composites filled with 10 phr of clay	
	Unmodified NC	Modified NC with ZS-DHDT
T_{s2} (min)	3.10	2.24
T_{90} (min)	4.44	3.92
M_H (dNm)	13.23	17.12
M_L (dNm)	3.50	4.27
M_H-M_L (dNm)	9.73	12.85

Morphology

Figure 3 illustrates the different morphologies of NR/SiO_2 composites after incorporating unmodified and modified NC. In the case of unmodified NC, agglomeration is evident, as shown in Figure 3(a). However, a smoother surface is observed when NC was modified using ZS-DHDT (Figure 3(b)). These differences explain the significant variation in the properties of the composites. The agglomeration of unmodified NC creates large defects between the filler surfaces and rubber molecules, reducing adhesion and impairing the material's ability to transfer stress. This leads to decreased mechanical properties, such as tensile strength and extensibility, due to the formation of high-stress points, making the composites prone to fracture under pressure. In contrast, the composite with modified NC shows uniformly distributed NC particles on the rubber surface, due to increased rubber-filler interaction and a significant reduction in filler agglomeration. This reduces defect regions within the composite matrix and dramatically enhances resistance to deformation under applied mechanical stress, as reflected in the improved properties of the composites.

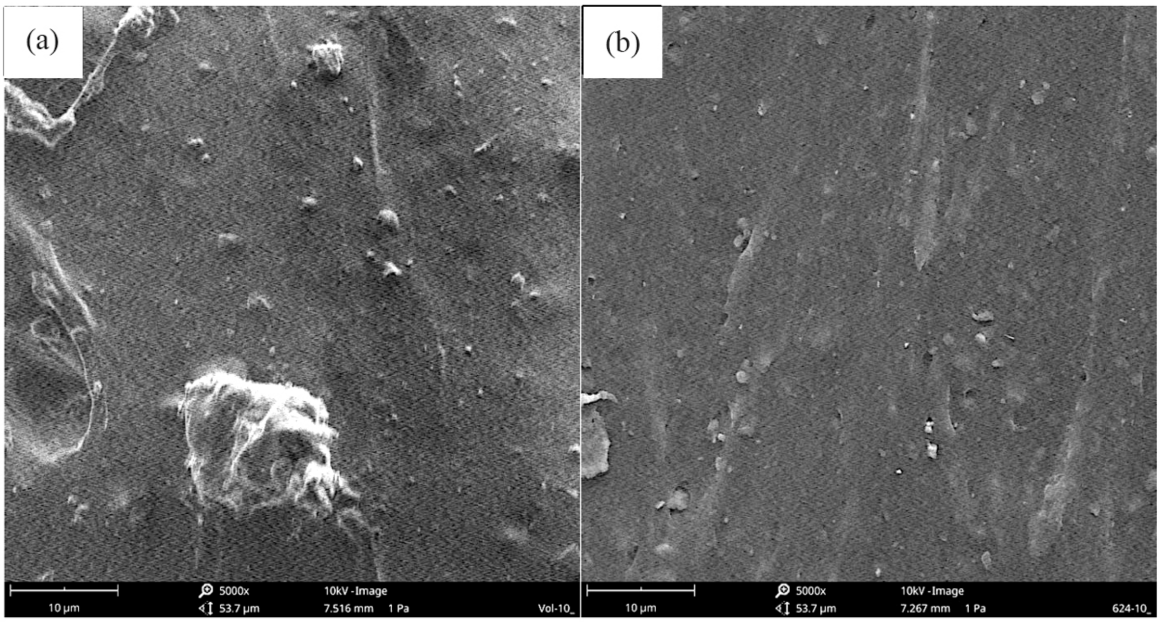

Figure 3 SEM images of the NR/SiO_2 composites filled with (a) unmodified NC and (b) modified NC.

Mechanical properties and Payne effect

The mechanical properties of NR/SiO_2 composites filled with bentonite clay and organoclay zinc are presented in Figure 4 and summarized in Table 4, along with the Payne effect. The tests revealed several improvements when using modified NC compared to unmodified NC. Specifically, the 100% and 300% moduli of the nanocomposites with organoclay zinc increased, indicating enhanced resistance to deformation at higher strains. Furthermore, the tensile strength and elongation at break were higher with organoclay zinc, highlighting better reinforcement and improved ductility in the rubber composites. These enhancements in rubber formulations using organoclay zinc are attributed to the clay modifiers (ZS and DHDT). These modifiers increase the spacing between silicate layers and reduce polarity, facilitating easier intercalation of NR between the clay layers, as seen in Figure 5. This improves interaction and bonding with the clay particles, ensuring uniform dispersion throughout the NR matrix. This prevents silica agglomeration, maintaining silica particles as individual entities dispersed evenly, thereby enhancing the overall mechanical performance of the composites. Moreover, the lower Payne effect observed in the modified NC composite indicates superior filler-filler interaction, suggesting better dispersion and interaction within the NR/SiO_2 matrix. These findings underscore the role of organoclay zinc in optimizing the mechanical properties and dispersion characteristics of NR/SiO_2 composites.

Table 4 Tensile properties and the Payne effect of the NR/SiO_2 composites filled with unmodified and modified NC with ZS-DHDT

Tensile properties	NR/SiO_2 composites filled with 10 phr of clay	
	Unmodified NC	Modified NC
Tensile strength (MPa)	24.05 ± 0.54	28.03 ± 0.47
Elongation at break (%)	763.85 ± 9.72	779.95 ± 32.98
100 % Modulus (MPa)	2.10 ± 0.03	2.68 ± 0.08
300 % Modulus (MPa)	6.73 ± 0.08	8.64 ± 0.32
Payne effect (KPa)	199.27	141.34

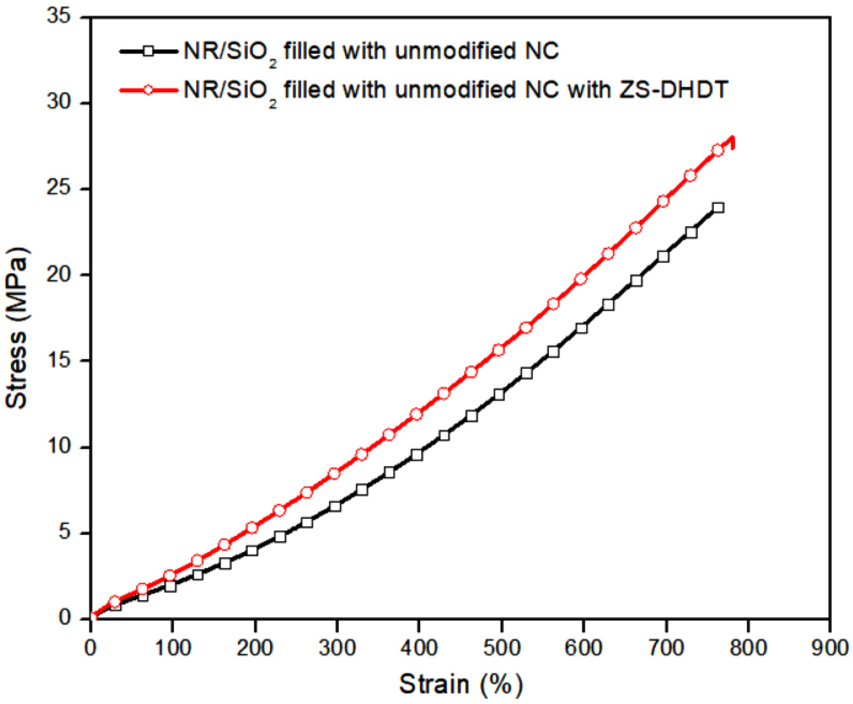

Figure 4 Stress-strain curves of the NR/SiO_2 composites filled with unmodified and modified NC with ZS-DHDT.

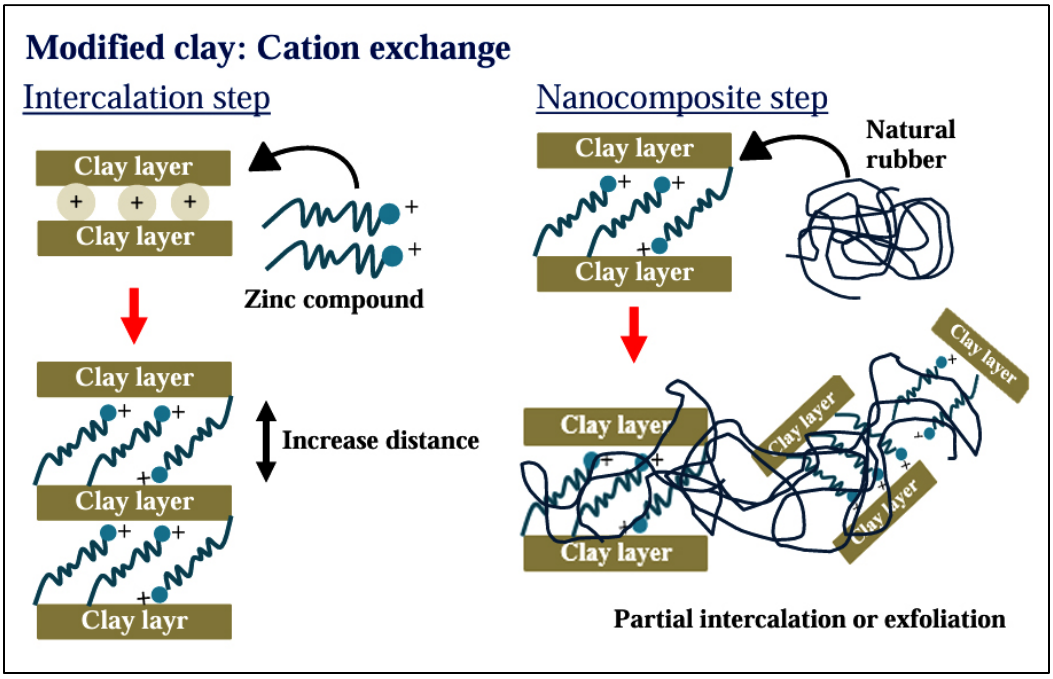

Figure 5 Cation exchange in modified clay: Intercalation and nanocomposite formation.

4. Conclusion

The study assessed the impact of unmodified clay versus clay modified with zinc stearate and a surfactant mixture (Zinc Organoclay) in NR composites. Zinc-based organoclay significantly increased the interlayer distance between clay particles, as confirmed by X-ray Diffraction (XRD) tests. This use of modified NC led to a reduction in both cure time and scorch time within 3.92 and 2.24 minutes, together with improved estimated crosslink density of 32.06%, tensile strength of 16.6%, modulus of 28.4% and Payne effect of 30.1%, reflecting enhancement of the filler-rubber interaction. These improvements are attributed to the surfactants expanding the spacing between clay particles, leading to better dispersion within the NR matrix. This advancement represents a significant technological development in material science, particularly for tire applications, by reducing wear resistance and extending product lifespan.

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References

[1] L. Bokobza, Natural rubber nanocomposites: A review, *Nanomaterials* **9** (2019) 12.

[2] N. Yan, J. K. Wu, Y. H. Zhan, H. S. Xia, Carbon nanotubes/carbon black synergistic reinforced natural rubber composites, *Plast. Rubber Compos.* **38** (2009) 290-296.

[3] S. Li, Z. Li, T. L. Burnett, T. J. A. Slater, T. Hashimoto, R. J. Young, Nanocomposites of graphene nanoplatelets in natural rubber: Microstructure and mechanisms of reinforcement, *J. Mater. Sci.* **52** (2017) 9558-9572.

[4] L. Xia, J. Song, H. Wang, Z. Kan, Silica nanoparticles reinforced natural rubber latex composites: The effects of silica dimension and polydispersity on performance, *J. Appl. Polym. Sci.* **136** (2019) 47449.

[5] R. E. Grim, Relation of the composition to the properties of clays, *J. Am. Ceram. Soc.* **22** (1939) 141-151.

[6] M. Galimberti, S. Agnelli, V. Cipolletti, "Hybrid filler systems in rubber nanocomposites," pp.349-414, In: Progress in Rubber Nanocomposites: Woodhead Publishing Series in Composites Science and Engineering, Eds. S. Thomas, H. J. Maria, Woodhead Publishing (2017).

[7] M. Sadeghalvaad, E. Dabiri, S. Zahmatkesh, P. Afsharimoghadam, Preparation and properties evaluation of nitrile rubber nanocomposites reinforced with organo-clay, $CaCO_3$, and SiO_2 nanofillers, *Polym. Bull.* **76** (2019) 3819-3839.

[8] M. M. Salehi, T. Khalkhali, A. R. Dourbash, Effect of simultaneous use of silica and nanoclay in rubber compounds based on nitrile rubber, *J. Rubber Res.* **21** (2018) 165-181.

[9] S. Vishvanathperumal, G. Anand, Effect of nanoclay/nanosilica on the mechanical properties, abrasion and swelling resistance of epdm/sbr composites, *Silicon* **12** (2020) 1925-1941.

[10] M. Sedničková, D. J. Mošková, I. Janigová, J. Kronek, L. Jankovič, M. Šlouf, I. Chodák, Properties of natural rubber composites with structurally different clay intercalable surfactants, *J. Polym. Res.* **24** (2017) 105.

[11] M. Lolage, P. Parida, A. Gupta, D. Rautaray, Synergistic effects of silica and nanoclay on curing characteristics, processing behaviour and mechanical properties of solution styrene butadiene rubber (SBR)–based tire tread compounds, *Emergent Mater.* **5** (2022) 957-966.

[12] L. Guy, S. Daudey, P. Cochet, Y. Bomal, New insights in the dynamic properties of precipitated silica filled rubber using a new high surface silica, *KGK-Kaut. Gummi Kunst.* **62** (2009) 383-391.

[13] M. I. Magzoub, I. A. Hussein, M. S. Nasser, M. Mahmoud, A. S. Sultan, A. Benamor, An investigation of the swelling kinetics of bentonite systems using particle size analysis, *J. Dispers. Sci. Technol.* **41** (2019) 817-827.

[14] H Agusnar, B. Wirjosentono, S Salim, T. Rihayat, T Fauzi, Synthesis and characterization of chitosan with addition of patchouli oil to improve mechanical properties biofilm, *J. Phys.: Conf. Ser.* **1116** (2018) 042001.

[15] S. H. Ismaeel, M. S. Mabrouk, A. A.-A. Ali, K. Abn-Elwalead, Synthesis and characterization of bentonite nanocomposites from egyptian bentonite clay, *Int. J. Nanotechnol. Allied Sci.* **1** (2017) 16-29.

[16] V. Sreedharan, P. V. Sivapullaiah, Effect of organic modification on adsorption behaviour of bentonite, *Indian Geotech. J.* **42** (2012) 161-168.

[17] P. Singla, R. Mehta, S. N. Upadhyay, Clay modification by the use of organic cations, *Green Sustain. Chem.* **2** (2012) 21-25.

[18] S. Sattayanurak, K. Sahakaro, W. Kaewsakul, W. K. Dierkes, L. A. E. M. Reuvekamp, A. Blume, J. W. M. Noordermeer, Elucidating the role of clay-modifier on the properties of silica- and silica/nanoclay-reinforced natural rubber tire compounds, *Express Polym. Lett.* **15** (2021) 666-684.

[19] L. E. Yahaya, K. O. Adebowale, B. I. Olu-Owolabi, Cure characteristics and rheological properties of modified kaolin-natural rubber composites, *Am. Chem. Sci. J.* **4** (2014) 472-480.

[20] P. Xia, H. Shao, A. He, Excellent oxygen barrier property of unfilled natural rubber/trans-butadiene-co-isoprene rubber vulcanizates under the synergistic effect of crosslinking density and crystallization, *Polymers* **16** (2024) 345.