TRENDS IN SCIENCES, 2024; 21(11): 8548 RESEARCH ARTICLE
https://doi.org/10.48048/tis.2024.8548

Comparative Study of Interfacial and Conventional Techniques for Nanosilica Incorporation in Natural Rubber Latex-Based Composites with Varied TEOS Content

Jindee Tuffrey*, Anuchit Wichianchom and Kwanruethai Boonsong

Faculty of Science and Technology, Rajamangala University of Technology Srivijaya, Nakhon Si Thammarat 80110, Thailand

(* Corresponding author's e-mail: jindee.t@rmutsv.ac.th)

Received: 9 June 2024, *Revised: 20 June 2024*, *Accepted: 24 June 2024*, *Published: 10 October 2024*

Abstract

This study investigates the preparation of natural rubber latex (NRL) composites with varying nanosilica contents of 5, 15, 30, and 45 phr, using both interfacial and conventional mixing techniques. Analysis focused on viscosity, plasticity, morphology, and FTIR spectra to evaluate the impact of these methods on composite properties. The interfacial technique maintained lower viscosity values, indicating better latex stability, and achieved higher silica yields and conversion rates (94 - 99%) at elevated TEOS contents. Plasticity analysis revealed that the interfacial method produced more uniform and stable plasticity values, suggesting improved resistance to oxidation and enhanced mechanical properties. SEM and FTIR analyses confirmed superior dispersion with the interfacial technique, especially at higher silica contents. These findings highlight the efficacy of the interfacial technique in optimizing the properties of NRL composites, making it a promising approach for advanced material applications.

Keywords: Interfacial, Silane, Natural rubber latex, Silica/Natural Rubber Nanocomposite, Masterbatch

Introduction

The development of silica-rubber composites has garnered significant attention in recent years due to their wide range of industrial applications, including tire manufacturing, automotive components, and engineering materials [1, 2, 3, 4]. These composites offer enhanced mechanical, thermal, and wear properties compared to conventional rubber materials, making them desirable for various engineering applications [1].

Previous methods for synthesizing silica-rubber composites predominantly involved mixing dry silica powder with rubber, which consumes significant energy and entails complex processing steps [5, 6]. Handling silica powder also poses operational challenges and safety risks due to its dust-like nature, necessitating stringent safety protocols and environmental controls [7]. In response, natural rubber latex (NRL)-based approaches have emerged as promising alternatives [1, 2], offering lower energy consumption and enhanced safety compared to dry mixing. These methods typically involve the use of silica powder, which undergoes mechanical deaggregation [8, 9, 10], surface modification of silica particles [11, 12],

modification of NRL itself [9, 12, 13], and destabilization of the wet composite through methods such as heat sputtering coagulation [9] or gas-assisted spray flocculation [12]. However, these methods still require additional energy, and concerns about safety persist due to the involvement of silica powder in modifying NRL and its operational use. Moreover, studies highlight the efficacy of silane-based silica precursors in improving silica-rubber compatibility and enhancing dispersion and interfacial adhesion [2], although detailed preparation methods remain underexplored [14, 15]. Conventional methods often employ vigorous mechanical stirring, which can lead to inadequate dispersion and compromised composite properties [16, 17, 18, 19, 20, 21].

In recent years, there has been renewed interest in in situ silane reactions within natural rubber latex (NRL), particularly via grafting facilitated by sodium dodecyl sulfate as an emulsifying agent [22]. Initial investigations using scanning electron microscopy (SEM) revealed silica particles of a few hundred nanometers, achieving a maximum silica content of 10 parts per hundred rubber (phr) with a conversion rate of approximately 80 - 90%. However, detailed documentation of the mixing reaction, presumed to involve conventional emulsion polymerization techniques with mechanical stirring, remains limited. Challenges persist in achieving optimal dispersion and stability, particularly at higher silica contents, where vigorous mechanical agitation can lead to latex destabilization [23] and incomplete silanization reactions. Our team's pioneering work on the interfacial reaction of tetraethyl orthosilicate (TEOS) and high ammonia natural rubber latex (HA-NRL) highlighted the 20% concentration as optimal for TEOS-mediated silica production, underscoring its potential for enhancing composite properties [24].

Our study builds upon these challenges and insights by employing an interfacial technique using TEOS as a silica precursor at varying concentrations. This approach aims to surpass mechanical stirring with an agitator by enhancing mechanical and thermal properties of the composites. We investigate optimal conditions for superior silica dispersion and loading through manipulation of silica content, meticulously examining parameters such as viscosity, silica yield, plasticity, morphological characteristics, and Fourier Transform Infrared (FTIR) analysis to comprehensively understand material properties. This research aims to advance composite material synthesis, providing insights into achieving high-performance silica/NR composites with potential industrial impact on improving rubber product quality and extending their service life.

Materials and methods

Materials

The 60%HA-NRL was purchased from Muang Mai Guthri PCL, Nakhon Si Thammarat, Thailand, and used as the polymer matrix. Deionized water was used to dilute 28% aqueous ammonia (AR grade, Qrec) to obtain a 0.7% aqueous solution, which was then used to dilute 60% HA-NRL to 20%. The silica precursor, TEOS, with a purity of 99% from Sigma-Aldrich, was used as received.

Composite preparation

The 20% HA-NRL was diluted with a 0.7% ammonia solution before mixing with TEOS. The silica content ($cSiO_2$), based on 100% TEOS conversion to silica, was varied at 5, 15, 30, and 45 phr. Two mixing techniques were used (see Figure 1): the conventional method with an agitator and the interfacial technique with a magnetic stirrer. In the interfacial method, TEOS was gradually added to form two layers, facilitating silica formation at their interface,

with the reaction in a closed system until the top layer disappeared, followed by 7 days of stirring. In the conventional method, TEOS was added at 1 mL/min to control the reaction aggressiveness. The composite's viscosity, plasticity, silica yield, morphology, and FTIR analysis were then characterized.

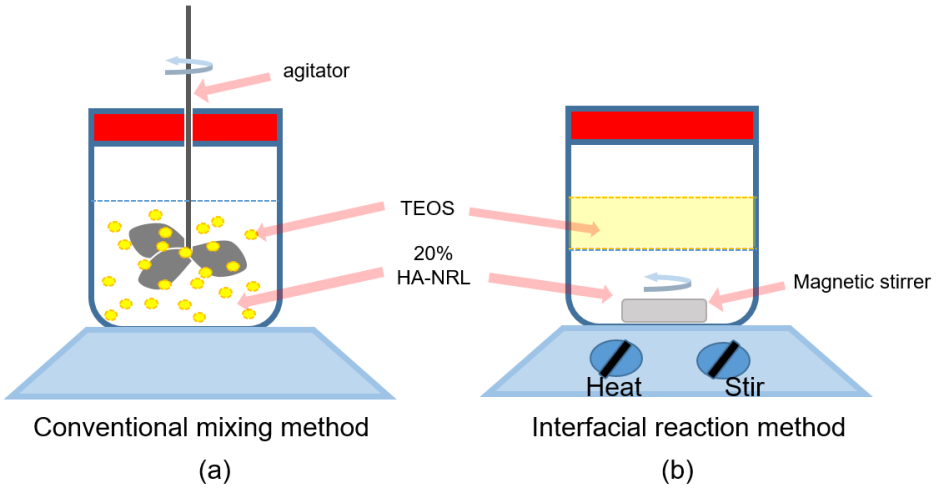


Figure 1: Illustration of the experimental set-up for this study: (a) conventional mixing method and (b) interfacial reaction method.

Properties determination

Viscosity

After the reaction was completed, the viscosity of the aqueous silica/NRL composite was assessed using Ford Cup No. 3 at room temperature, following the guidelines outlined in ASTM-D1200 [25]. The viscosity measurements were recorded in seconds and then converted to Centistokes (cSt) using Gardco Application Version 1.0.3.

Silica yield

After the reaction was completed, composite films were prepared by applying the mixture onto glass plates and then oven-dried at $105 \pm 3\ ^{o}C$ until completely dried. These samples were also used for morphological studies. The ash content, representing the silica content of the dried composite films, was determined in accordance with ASTM-D297 [26] using a Cabolite furnace. The silica yield, expressed in parts per hundred rubber (phr), was calculated using Equation 1, while the percentage of silica conversion was determined using Equation 2. Here, W_1 denotes the mass of actual silica in the sample, W_2 represents the mass of the sample, and W_3 signifies the mass of the theoretical amount of silica in the sample.

$$SiO_2(phr) = \left(\frac{W_1}{W_2 - W_1}\right) * 100 \quad (1)$$

$$Conversion(\%) = \left(\frac{W_1}{W_3}\right) * 100 \quad (2)$$

Plasticity

Due to a wide range of dry composite viscosities, conventional techniques using a Mooney viscometer were unlikely to be suitable. Therefore, the rapid plasticity of the sample was assessed to examine the impact of the composite preparation method on the viscosity or hardness of the green (unvulcanized) composite, employing the MonTech Rapid Plastimeter following ISO 2007 standards [27]. The Plasticity Retention Index (PRI) was then computed using Equation 3, where the plasticity value before aging is denoted as P_0, and P_{30} represents the plasticity value before and after aging the sample at 140 ^oC for 30 minutes, respectively.

$$PRI = \left(\frac{P_{30}}{P_0}\right) * 100 \tag{3}$$

Morphological study

The dried composite film was deep-frozen using liquid nitrogen and then fractured. A thin gold (Au) coating of approximately 10 μm was sputter-deposited onto the sample. The analysis was performed using a Zeiss Field Emission Scanning Electron Microscope (FE-SEM) operating at an accelerating voltage of 2.00 kV and an aperture size of 30 μm.

FTIR Analysis

FTIR analysis was conducted using the Attenuated Total Reflectance (ATR) method to assess silica dispersion in NRL composite films, which were directly analyzed using a DRY-CABINET Model AD-030 spectrometer equipped with an ATR accessory. Spectra were recorded in the range of 4000-400 cm^{-1} with a resolution of 4 cm^{-1}, averaging 32 scans for each sample.

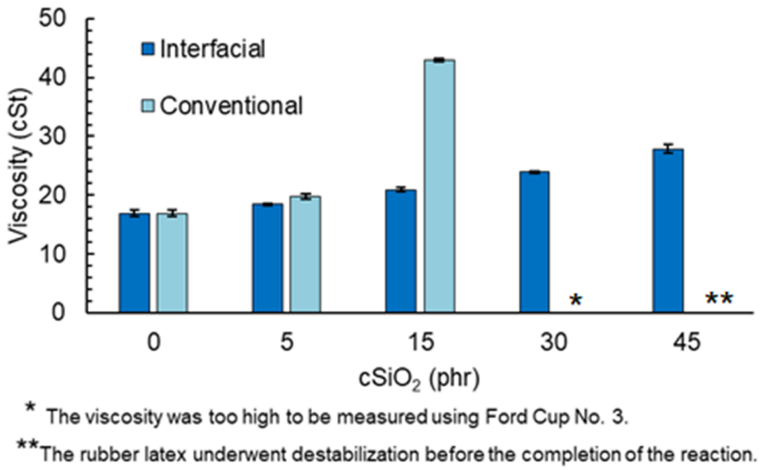
Results and discussion

Viscosity

Figure 2 shows that the viscosity of the aqueous silica/NRL composites increased with higher silica content for both preparation methods; however, the interfacial technique maintained lower and more stable viscosity levels, indicating better latex stability. This stability prevents latex destabilization and ensures a smoother, more controlled reaction process, which is crucial for the consistent quality of the composite material. In contrast, the conventional method led to significant viscosity increases at higher silica loadings, causing latex destabilization and incomplete reactions, attributed to latex particle dehydration during the silanization reaction of TEOS with water and ammonia in NRL [28]. The gradual reaction in the interfacial method prevented silica particle aggregation, unlike the faster kinetics and clustering observed in the conventional method [23, 29]. These insights into stability and efficiency help optimize the preparation process for producing more consistent and high-quality composite materials.

Silica yield

Figure 3 indicates that both methods yielded similar amounts of silica at low concentrations. However, at higher concentrations, the interfacial technique showed an increasing trend in silica yield and higher conversion rates (ranging from 94% to 99%). This is because higher TEOS contents require longer reaction times, resulting in increased silica yield [30]. In

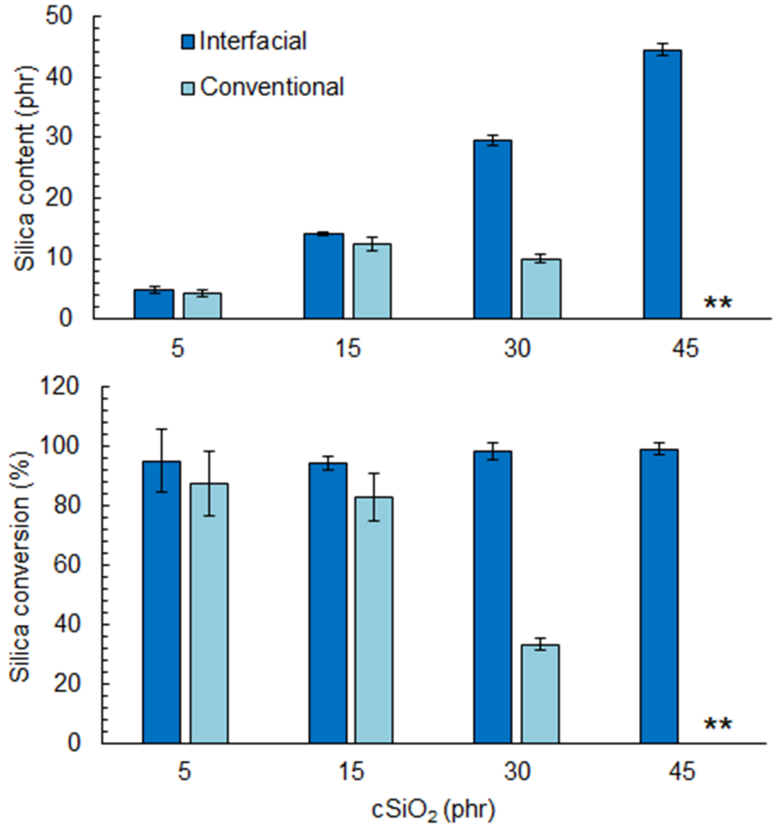


* The viscosity was too high to be measured using Ford Cup No. 3.

**The rubber latex underwent destabilization before the completion of the reaction.

Figure 2: Effect of composite preparation methods and $cSiO_2$ contents on the viscosity of silica/NRL composites.

contrast, the conventional method struggled with latex instability, limiting TEOS incorporation to 15 phr of $cSiO_2$ and achieving lower conversion rates (87%). The interfacial method's ability to achieve higher silica yields, particularly at higher TEOS concentrations, indicates more efficient utilization of precursor materials. This efficiency not only translates to better reinforcement of the composite with silica but also highlights the economic and sustainable advantages of the interfacial method for NRL composite production.



**The rubber latex underwent destabilization before the completion of the reaction.

Figure 3: Effect of composite preparation methods and $cSiO_2$ contents on the silica yields of silica/NR composites.

Plasticity

The plasticity properties of the composite provide valuable insights into its mechanical behavior, particularly its hardness and ability to maintain shape under load. These properties reflect the dispersion of silica particles and the silica content within the natural rubber matrix, with higher plasticity typically associated with better dispersion and/or higher silica content [31, 32, 33, 34]. Plasticity results (Figure 4) demonstrate that P_o values of the composite using the conventional method at low $cSiO_2$ contents (5-15 phr) were slightly better than those using the interfacial method, despite the latter's higher yields. This could be due to the conventional method producing more irregularly shaped silica aggregates, which increased the viscosity and hardness of the rubber/silica composite [35]. However, as silica content increased, the PRI values deteriorated in the conventional method due to poorer dispersion of TEOS in NRL, leading to lower silica conversion and reduced rubber-filler interaction.

Conversely, composites prepared with the interfacial method demonstrated superior plasticity, particularly at higher silica loadings. This enhancement in plasticity correlates with improved mechanical properties such as hardness and shape retention under load, indicating better dispersion of silica within the natural rubber matrix and increased resistance to oxidation at elevated temperatures [36], attributed to silica's thermal enhancement effect in the rubber matrix. These findings underscore the effectiveness of the interfacial technique in producing composites with superior plasticity and mechanical properties. The interfacial method's capability to achieve higher yields and better dispersion at increased silica contents highlights its potential for optimizing NRL composite manufacturing, thereby enhancing materials with superior performance characteristics suitable for diverse applications. These insights are pivotal for advancing NRL composites with enhanced mechanical stability and reliability.

Morphology

SEM analysis (Figure 5) highlighted the superior dispersion achieved through the interfacial method. While both techniques initially showed comparable dispersion at lower silica contents (5 phr), the interfacial method maintained superior dispersion as the silica content increased to 15 phr and beyond, contrasting with significant aggregation observed in the conventional method. Particularly notable was the observation of a distinctive flake-like silica structure at 30 phr using the interfacial technique (Figure 6a), suggesting potential benefits from optimized flow patterns, stirring speeds, and silica formation rates. Further investigation is needed to fully grasp this phenomenon and its implications for composite properties. Additionally, SEM analysis depicted silica particles in the range of a few tens of nanometers (Figure 6b). These findings underscore the critical influence of composite preparation methods and TEOS content on viscosity, plasticity, and morphology, advancing our understanding of their interconnected roles in composite development.

FTIR spectra

FTIR analysis (Figure 7) of the composites reveals significant insights into dispersion and interaction of silica within the rubber matrix. Composites prepared using the interfacial technique exhibit more distinct and higher absorption silica peaks in the Si-O-Si asymmetric stretching region (1000-1250 cm^{-1} [37]), indicating superior dispersion compared to those prepared conventionally. Despite slightly broader peaks at higher silica contents, suggesting some variability in dispersion within the NR matrix, overall dispersion remains superior. In contrast, the conventional method shows sharp silica peaks at lower silica content but

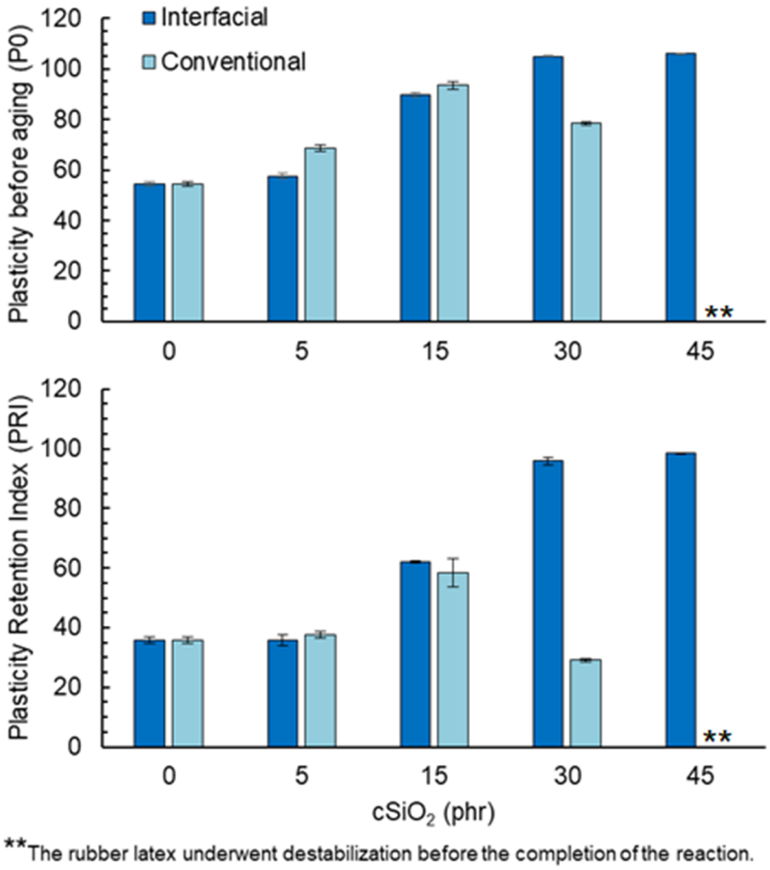


Figure 4: Effect of composite preparation methods and $cSiO_2$ contents on the plasticity of silica/NR composites.

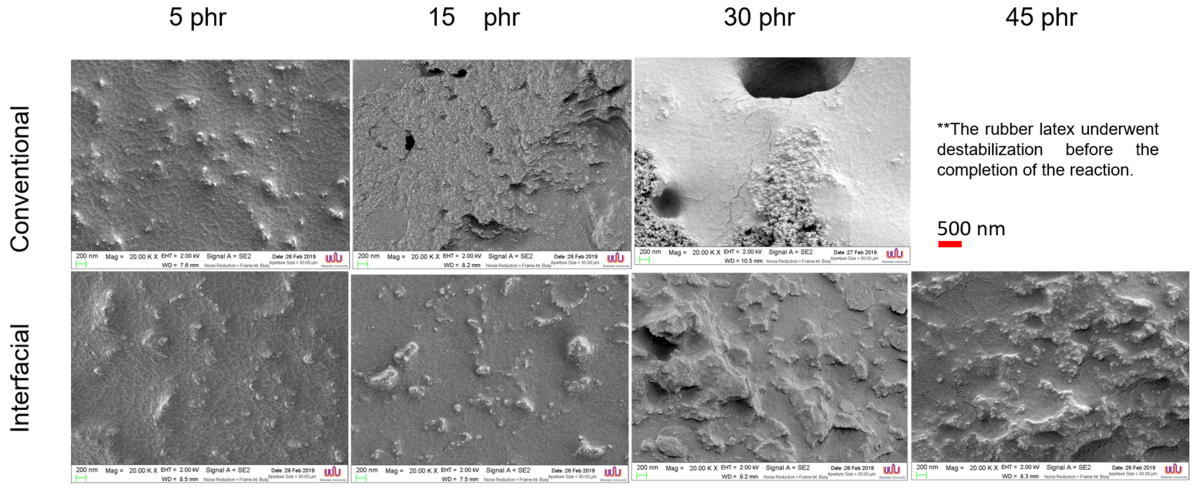


Figure 5: SEM micrographs of silica/NR composites prepared using conventional and interfacial methods and varied $cSiO_2$ contents.

broader peaks at higher concentrations, indicating poorer dispersion that aligns with SEM findings. Notably, FTIR analysis at 5 phr silica confirms superior dispersion with the interfacial method, underscoring its advantage over SEM in assessing dispersion quality and reinforcing its efficacy in enhancing composite properties through improved silica dispersion and interaction within the rubber matrix.

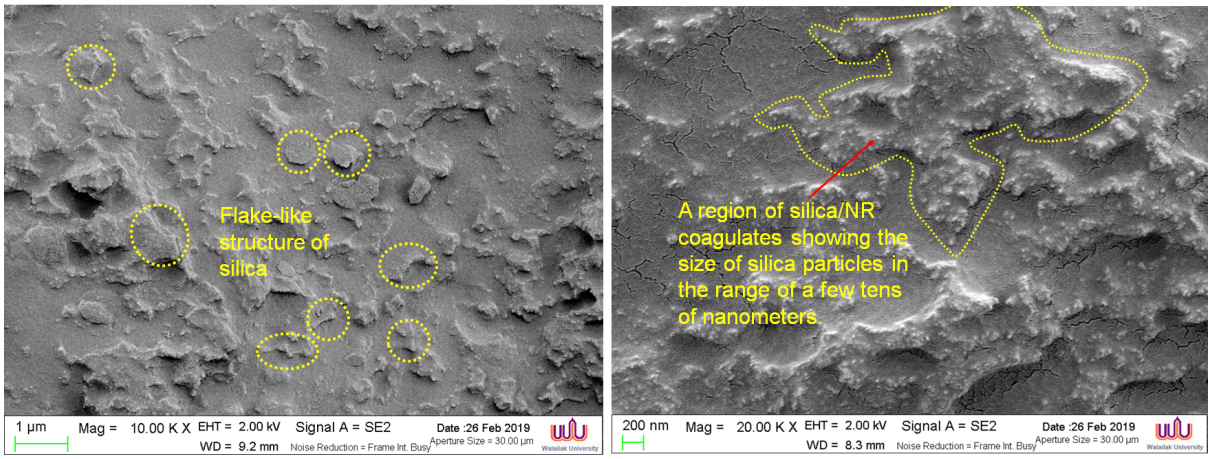


Figure 6: SEM micrographs depicting the morphology of silica using the interfacial technique: (a) flake-like silica observed in the sample with 30 phr of $cSiO_2$, and (b) dispersion of nanosilica, a few tens of nanometers in size, within the silica/NR coagulates in the sample with 45 phr of $cSiO_2$.

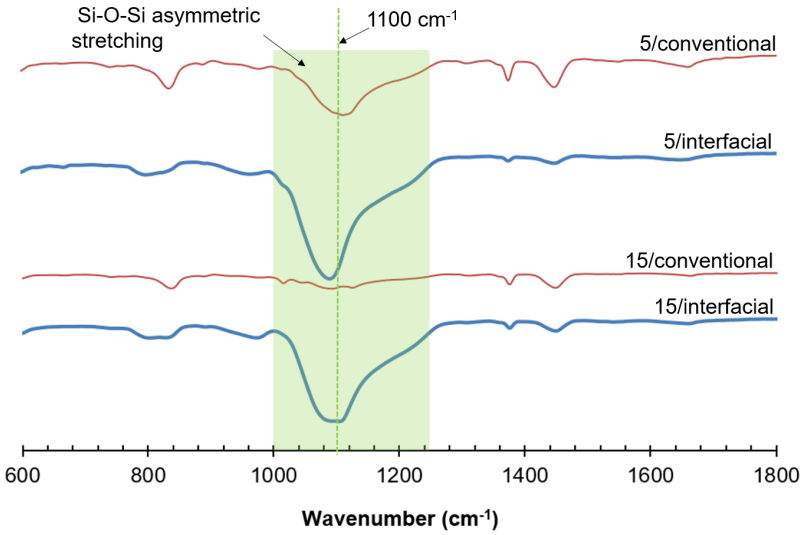


Figure 7: FTIR spectra of silica/NR composite prepared using conventional and interfacial methods varying $cSiO_2$ contents at 5 and 15 phr.

Proposed silanization mechanisms of TEOS and NRL within conventional and interfacial methods

As shown in Figure 8, the mechanical processing route generates a more aggressive environment, compelling the TEOS phase to disperse within the latex phase through mechanical means. Since TEOS is less polar compared to the NRL phase, they are immiscible, leading to the formation of TEOS droplets within NRL. The size of these droplets varies based on agitation speed. Silanization takes place at the interface of these TEOS droplets and NRL, involving a reaction with ammonia and water [38] (see Equation 4). These components typically serve as stabilizers for NR particles [39]. Furthermore, the products of silica oligomer and ethanol resemble water-like species, contributing to the destabilization process of NRL [29]. The aggressiveness or rate of this phenomenon can be heightened by higher concentrations of ammonia, NRL, and TEOS. However, slowing down this reaction by confining it to

occur only at the interface of TEOS/NRL layers allows the growing silica oligomer to disperse gradually in the latex, preventing the loss of water and ammonia too quickly. This extended reaction time facilitates the uniform conversion of silica and better dispersibility. Consequently, this controlled approach results in a more stable system with uniform composites, improved dispersion, and the capacity to prepare higher silica content without significantly escalating the viscosity of the system.

$$Si(OC_2H_5)_4 + 2H_2O \xrightarrow{NH_3} SiO_2 + 4C_2H_5OH \quad (4)$$

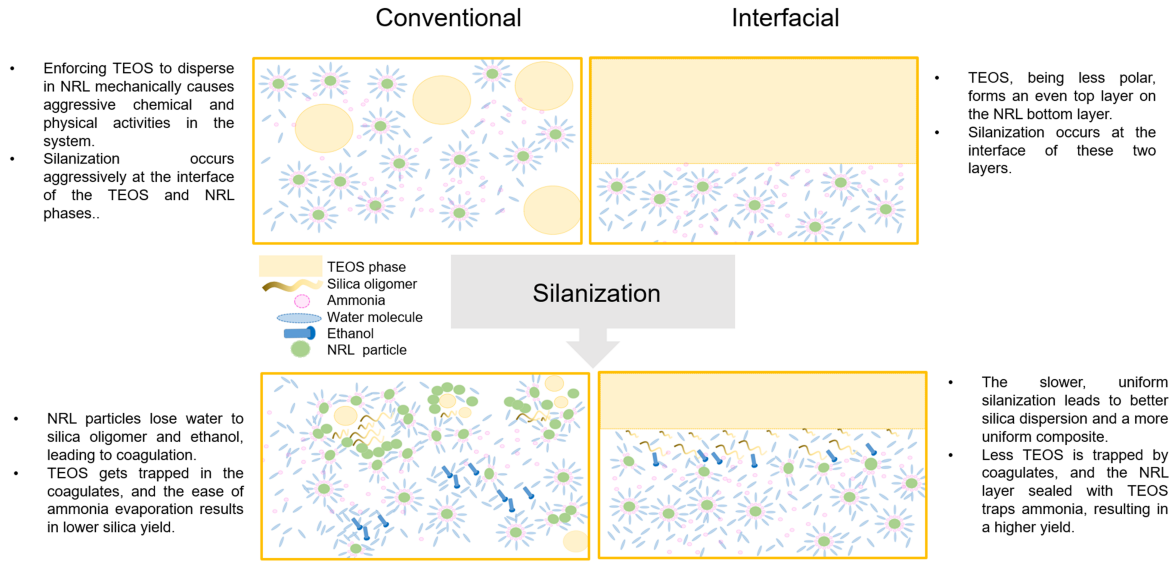


Figure 8: Illustration of the proposed silanization mechanisms of TEOS and NRL using conventional and interfacial methods.

Conclusions

The study demonstrated that the interfacial mixing technique significantly enhances the properties of NRL composites with varying nanosilica contents. This method maintained lower viscosity values, indicative of better latex stability, and achieved higher silica yields and conversion rates (94 - 99%) at higher TEOS contents, compared to the conventional method, which faced issues with latex destabilization and lower conversion rates. Plasticity analysis showed more uniform and stable values with the interfacial method, indicating improved resistance to oxidation and enhanced mechanical properties. SEM analysis confirmed superior dispersion with the interfacial technique, particularly at higher silica contents. FTIR analysis further supported these findings, showing narrower peaks and higher absorption in the Si-O-Si asymmetric stretching region (1000 - 1250 cm^{-1}) with the interfacial method, while the conventional method exhibited broader peaks at higher silica contents, indicating poorer dispersion. These results underscore the potential of the interfacial technique for producing high-performance NRL composites, offering significant advantages over conventional methods.

Acknowledgements

The authors gratefully acknowledge the support of Rajamangala University of Technology Srivijaya for funding this research. We would like to thank Mr. Surasak Raksrithong for facilitating the use of instruments.

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