Development of Natural Zeolite-Based Rubber Compounds for Water Sealing Applications

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Received: 1 April 2026 | Revised: 27 April 2026 | Accepted: 4 May 2026

ABSTRACT

This study examines the usage of natural zeolite as a substitute for silica in rubber compounds used for hydraulic sealing. Zeolite was modified by acid activation followed by thermal treatment to enhance its surface properties and structural stability. X-Ray Fluorescence (XRF) analysis revealed an increase in the SiO_2 content to up to 60.4 wt% after modification. Scanning Electron Microscopy (SEM) demonstrated a more uniform particle morphology, while Fourier Transform Infrared (FTIR) spectroscopy confirmed that the aluminosilicate framework was preserved. Rubber compounds based on synthetic isoprene (SKI-3) were prepared by replacing 5–20 phr of silica with the modified zeolite while maintaining constant filler loading. Increasing the zeolite content slightly decreased Mooney viscosity (from 44 to 41 MU), indicating improved processability. Tensile strength decreased moderately, from 13.54 MPa to 12.98 MPa, remaining within the required industrial specification of ≥12 MPa. Elongation at break increased, and tear resistance remained above the acceptable limit, showing that modified natural zeolite can be used as a functional mineral filler in sealing elastomers without significantly deteriorating key performance properties. Up to 20 phr of precipitated silica can be replaced while maintaining compliance with industrial requirements, offering a cost-effective, sustainable alternative for rubber compound formulation.

Keywords-natural zeolite; rubber composites; mineral fillers; filler replacement; elastomer reinforcement; hydraulic seals; acid modification; physicomechanical properties

I. INTRODUCTION

The mechanical performance of filled elastomers is governed by polymer-filler interactions and the formation of filler networks within the rubber matrix [1]. The spatial organization and aggregation of filler particles also play a key role in determining mechanical behavior and deformation characteristics [2]. Precipitated silica is one of the most widely used reinforcing fillers due to its high surface area and silanol groups, which promote interaction with polymer chains [3]. However, silica-filled systems are characterized by strong filler-filler interactions that lead to the formation of a developed filler network and increased compound viscosity [4]. In order to improve compatibility with nonpolar elastomers, silane coupling agents are commonly used to enhance interfacial bonding [5]. Developing alternative mineral fillers has become an important area of research due to the need to reduce costs and improve the sustainability of rubber materials [6]. Among natural aluminosilicates, zeolites are of particular interest due to their crystalline structure, ion-exchange properties, and thermal stability [7]. Researchers have also explored the development of composite materials incorporating recycled rubber in cement-based systems. The addition of crumb rubber and polymer fibers has enhanced energy absorption and fracture resistance [8]. Authors in [9] showed that using zeolites can influence the curing behavior and mechanical performance of elastomer composites. At the same time, the reinforcing efficiency of zeolites depends on their surface characteristics and how well they disperse within the polymer matrix [10]. Despite these findings, the application of natural clinoptilolite in industrial rubber formulations remains understudied. In particular, comparative studies performed under identical processing conditions without coupling agents are lacking. Coupling agents are necessary to evaluate the intrinsic reinforcing behavior of mineral fillers. This study examined the usage of natural zeolite from the Chankanai deposit as a partial mineral component. A comparison with precipitated silica was carried out under non-silanized conditions to isolate the intrinsic reinforcing behavior of mineral fillers. The objective was not to propose a universal silica substitute, but rather to evaluate zeolite's performance within a defined compound formulation relevant to industrial practice.

II. MATERIALS AND METHODS

A. Materials

Natural clinoptilolite zeolite from the Chankanai deposit was used as the primary mineral filler. Prior to treatment, the mineral was crushed and sieved mechanically to produce fractions below 100 μm. The base elastomer was SKI-3 isoprene rubber with a Mooney viscosity of ML(1+4) at 100°C: 70 ± 5 MU. Commercially available precipitated silica with a specific surface area of 160–180 m²/g (BET) served as the reference filler. Carbon black P-220 was used as a secondary reinforcing agent. The standard industrial-grade compounding ingredients included zinc oxide (ZnO), stearic acid, a sulfenamide accelerator, antioxidants, processing oil, pine rosin, and protective wax.

B. Preparation of Modified Zeolite

The zeolite modification process included a two-stage acid-thermal treatment. First, the powder was treated with 0.5-2 N aqueous hydrochloric acid at a solid-to-liquid ratio of 1:10. The suspension was stirred at 75-80°C (300 rpm) in three consecutive stages (3 h, 2 h, and 1 h), with filtration and washing with distilled water performed between stages until chloride ions were eliminated (confirmed by $AgNO_3$). The acid-activated samples were then air-dried and calcined in a muffle furnace at temperatures ranging from 100 to 800°C (heating rate: 5°C/min; dwell time: 2 h) to stabilize the structure.

C. Compound Preparation and Vulcanization

Rubber compounds were prepared in an internal laboratory mixer with a 1.5 L chamber and a rotor speed of 40 rpm. The 10-min mixing cycle began with 2 min of rubber mastication at 50 °C. Then, fillers and processing aids were gradually added while maintaining a temperature below 110 °C. Curatives were incorporated on a two-roll mill at 50–60 °C. Vulcanization was performed in a hydraulic press at 155 °C and 10 MPa for 15 min. This duration was determined by preliminary rheometric analysis to ensure optimal crosslinking. Samples were conditioned at 23 ± 2 °C for 24 h before testing.

D. Characterization and Testing

A structural analysis of the fillers was conducted using X-Ray Fluorescence (XRF), Fourier-Transform Infrared spectroscopy (FTII) (Thermo Scientific Nicolet iS10, 400–4,000 cm^(−1), KBr pellets), and Scanning Electron Microscopy (SEM) (JEOL JSM-6510LV, 15 kV, gold-coated samples). Processability was evaluated via Mooney viscosity (ML 1+4 at 100°C). The mechanical properties, including tensile strength, elongation at break, and tear resistance, were determined using a universal testing machine at a crosshead speed of 500 mm/min. Shore A hardness was measured using a durometer. Climatic aging resistance was assessed by monitoring changes in elongation after exposure to elevated temperature and humidity for 72 h. All reported values represent the average of at least three independent measurements, and the experimental error for the measured properties did not exceed ±5%.

III. RESULTS AND DISCUSSION

A. Structural and Chemical Characteristics of Zeolite

Figure 1 shows the structural characteristics of thermally treated natural and acid-modified zeolite compared to commercial precipitated silica. Thermal treatment within the investigated temperature range did not cause structural instability in the zeolite phase. After calcination, the material retained its characteristic framework, indicating sufficient thermal resistance for rubber processing conditions. In contrast, precipitated silica exhibits the typical behavior of an amorphous material. The increase in SiO_2 content observed after acid treatment, together with slight changes in Al_2O_3 concentration, indicates partial dealumination of the zeolite framework. This process increases the Si/Al ratio and is associated with changes in surface acidity and active sites. These modifications can affect the interaction between the mineral filler and the elastomer matrix, potentially improving interfacial compatibility. The quantitative XRF results are summarized in Table I. The data show a gradual increase in relative SiO_2 content with increasing treatment severity. For natural zeolite, the SiO_2 content rises from 58.0 wt% at 100°C to 59.9 wt% at 400°C. After acid activation and calcination, the silica content increases to 60.4 wt%. This increase is due to dehydration and the partial removal of non-siliceous components during the acid treatment process. The slight variation in Al_2O_3 content suggests partial dealumination, which increases the Si/Al ratio. This modification is expected to influence surface activity and affect interfacial interactions in elastomer systems. Unlike precipitated silica, which consists almost entirely of amorphous SiO_2 (97.2 wt%), zeolite has a multicomponent mineral composition. This compositional complexity implies that zeolite's reinforcing action may rely not only on surface chemistry, but also on the rigidity of the aluminosilicate framework.

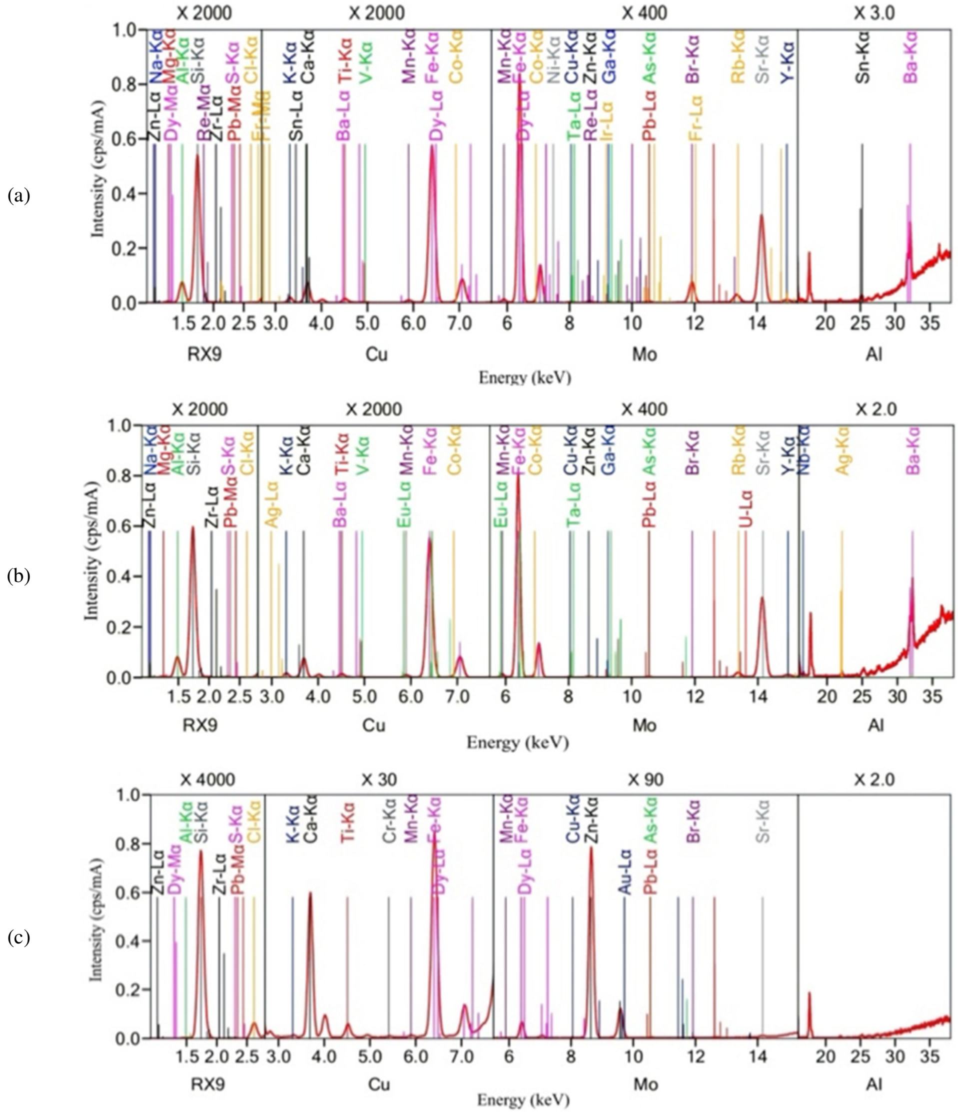


Fig. 1. XRF elemental composition of thermally treated: (a)natural zeolite, (b) acid-modified zeolite, and (c) commercial precipitated silica.

TABLE I. ELEMENTAL COMPOSITION OF CALCINED NATURAL ZEOLITE, ACID-MODIFIED ZEOLITE, AND PRECIPITATED SILICA (WT%)

Main component	**Natural zeolite, wt%**		**Modified zeolite, wt%**		**Precipitated silica, wt%**
	100°C	400°C	300°C	400°C	
SiO_2	58.0	59.9	58.0	60.4	97.21
Al_2O_3	15.8	16.3	15.4	16.3	0.495
CaO	6.76	6.94	6.70	6.77	0.675
Fe_2O_3	6.20	6.48	5.98	6.10	0.094

B. Morphological Analysis

Figure 2 illustrates the surface morphology of the thermally treated zeolite samples. Natural zeolite that has been treated at 100°C, as portrayed in Figure 2 (a), exhibits irregular agglomerates with a porous, layered appearance. The surface is relatively heterogeneous, and interparticle voids are visible. After undergoing acid modification followed by calcination at 300°C, as displayed in Figure 2 (b), the particles appear cleaner and more uniform. This change likely reflects the removal of loosely bound impurities and the partial restructuring of the external surface. At 400°C, as presented in Figure 2 (c), the morphology becomes slightly denser, though the particles' integrity remains intact. No signs of melting or collapse are observed. This stability is important for maintaining filler performance during compounding and vulcanization. The improved surface uniformity after treatment may reduce agglomeration tendencies and contribute to the observed processing behavior in rubber compounds.

C. Fourier Transform Infrared Analysis

Figure 3 shows the FTIR spectra of thermally treated natural and modified zeolites. All spectra demonstrate a strong absorption band between 1000 and 1100 cm^{-1}, which corresponds to the asymmetric stretching vibrations of the Si-O-Si bonds. The persistence of this band indicates that the silicate backbone remains intact after acid treatment and calcination. Bands in the 450–550 cm^{-1} range are associated with bending vibrations of Si-O and Al-O bonds within the tetrahedral framework. Slight changes in intensity are observed in acid-treated samples, which are consistent with partial dealumination, as indicated by the XRF results. The characteristic framework bands do not disappear after calcination up to 400°C, suggesting that the zeolite's structure remains stable at processing temperatures.

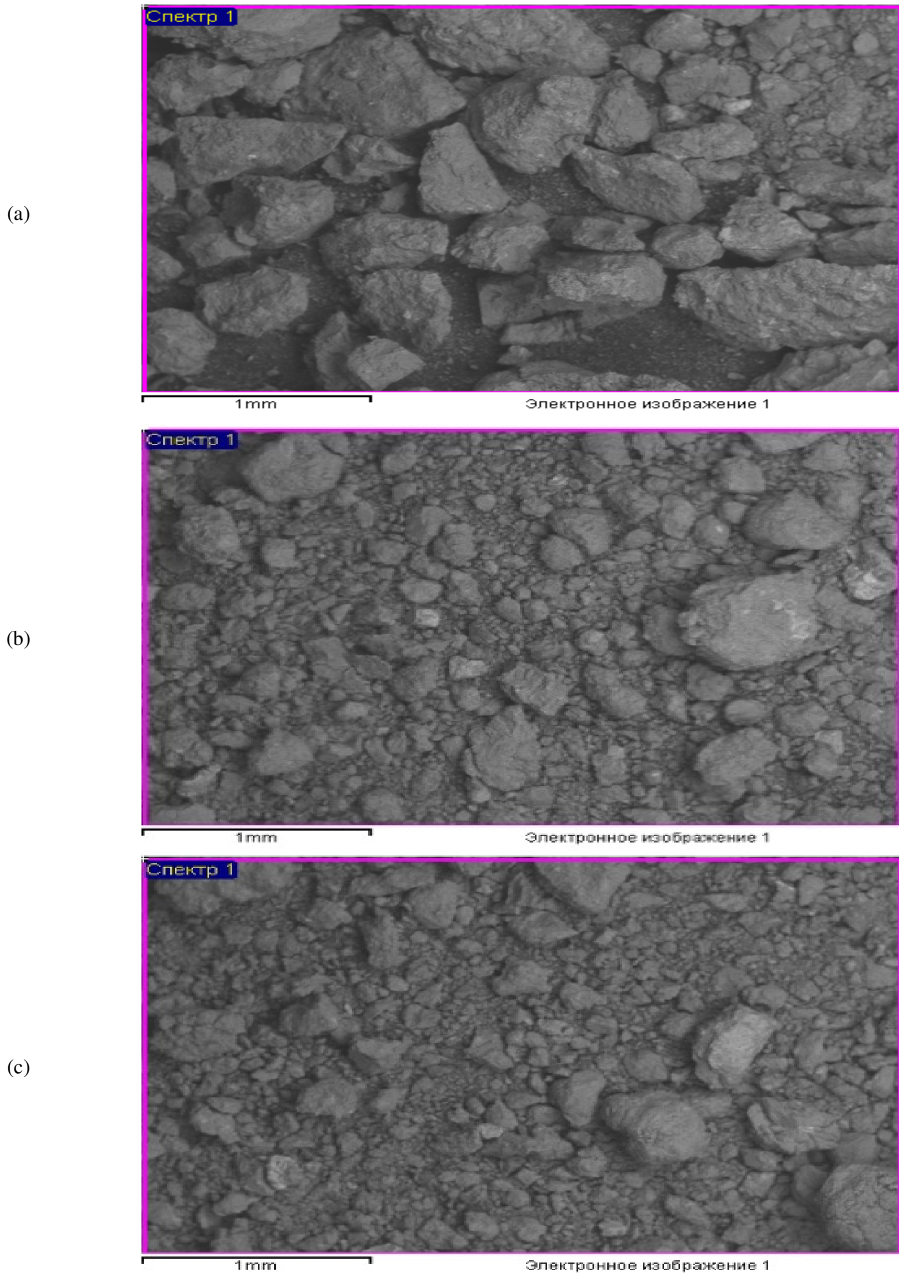
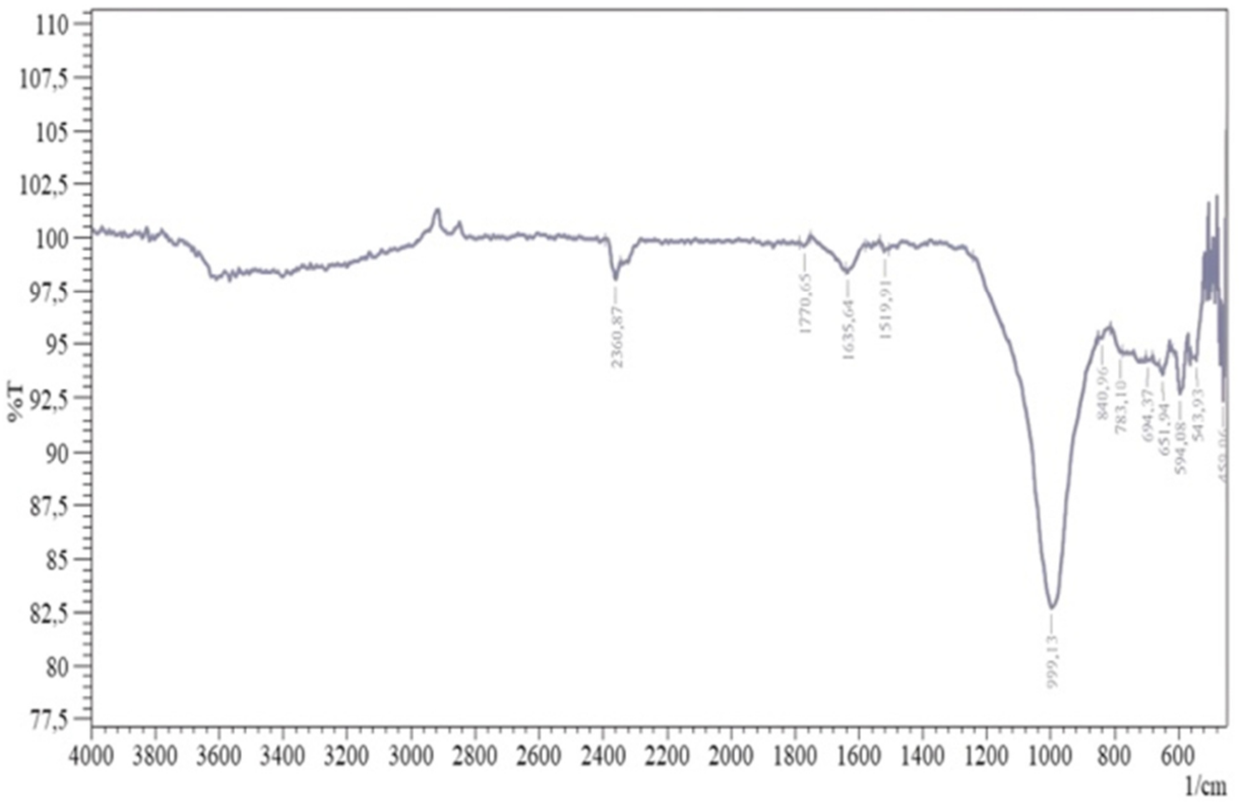


Fig. 2. SEM micrographs of: (a) natural zeolite after calcination at 100 °C, (b) acid-treated zeolite at 300 °C, (c) acid-treated zeolite at 400 °C.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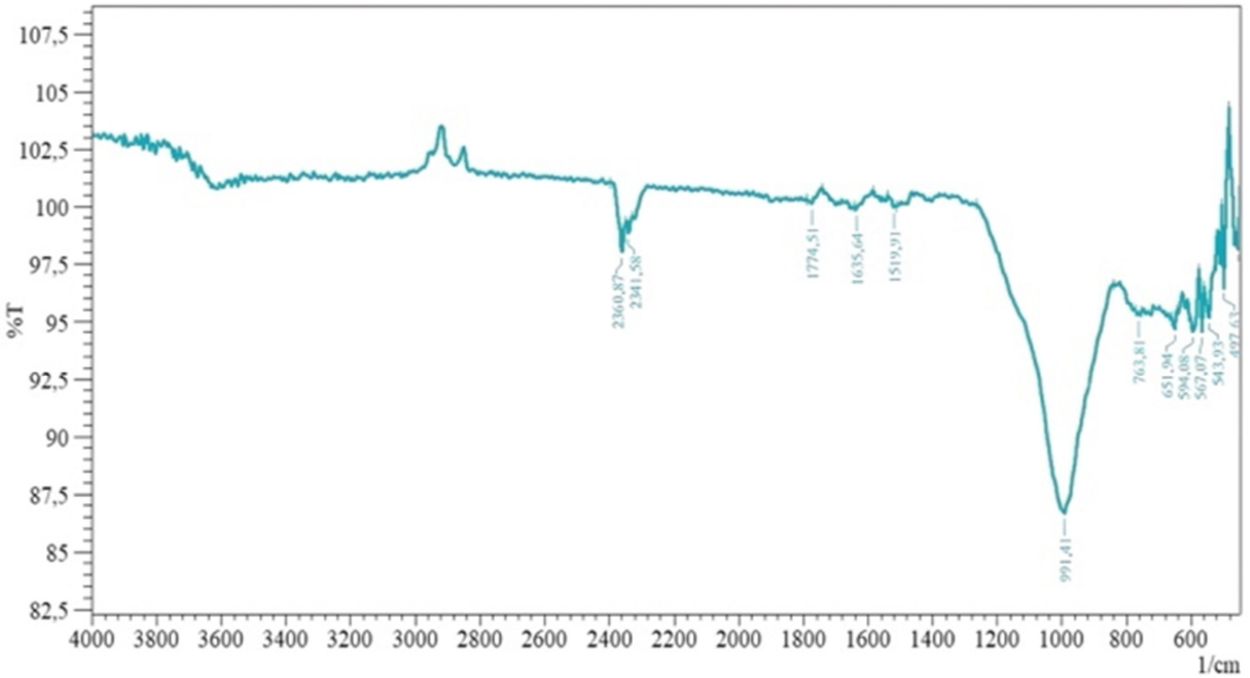
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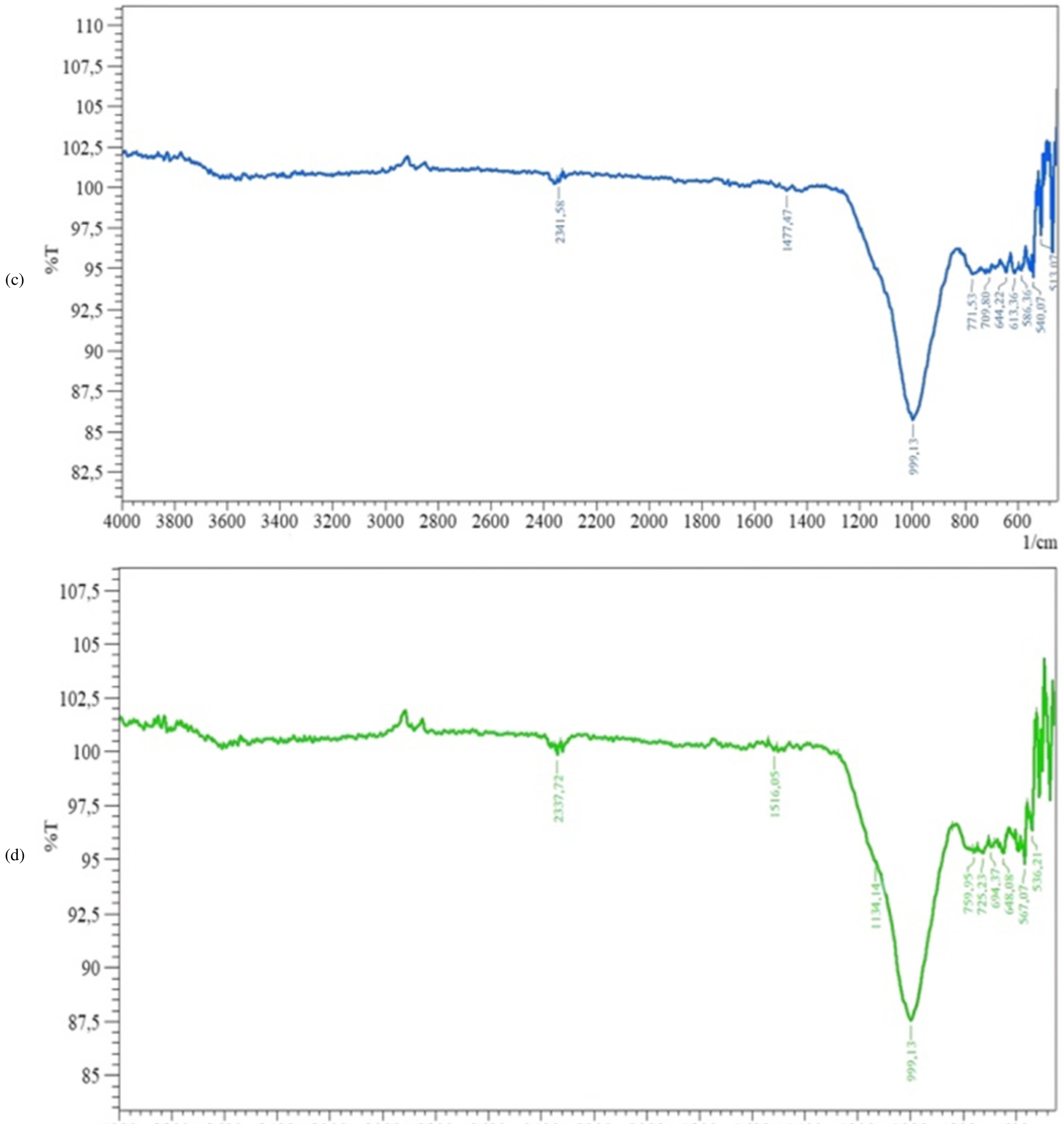

Fig. 3. FTIR spectra of thermally treated zeolite samples: (a) natural zeolite after calcination at 100 °C, (b) natural zeolite after calcination at 400 °C, (c) acid-treated zeolite after calcination at 300 °C, (d) acid-treated zeolite after calcination at 400 °C.

These observations further support the conclusion that acid-thermal treatment modifies the zeolite's surface characteristics without destroying its crystalline framework. The preservation of the main structural bands, coupled with subtle intensity changes, indicates surface-level modification rather than bulk structural degradation.

D. *Effect of Zeolite Content on Rheological and Mechanical Properties*

The formulation of the investigated rubber compounds is presented in Table II. The total filler loading remained constant at 208 phr for all compositions. Precipitated silica was gradually replaced with acid-treated zeolite at levels ranging from 5 to 20 phr, while maintaining the same amounts of base rubber, carbon black P-220, curatives, and processing additives. This approach enables the direct evaluation of the impact of filler substitution, independent of formulation alterations. The reduction in Mooney viscosity indicates a less developed filler network compared to silica-filled systems. This behavior can be attributed to zeolite particles' lower tendency to form strong agglomerated structures, unlike precipitated silica, which forms them due to hydrogen bonding between silanol groups. Consequently, improved processability can be achieved, which is advantageous in industrial mixing and shaping operations. Unlike silica, which forms a highly developed filler network due to hydrogen bonding between silanol groups, zeolite particles exhibit weaker interparticle interactions, resulting in reduced structure formation.

The rheological and mechanical properties of the prepared rubber compounds and vulcanizates are summarized in Table III. As the zeolite content increases, a gradual decrease in Mooney viscosity from 44 to 41 units is observed. This behavior indicates a less pronounced structure-forming effect than that of precipitated silica, resulting in improved processability. The reinforcing behavior of mineral fillers in rubber systems depends on chemical composition, particle morphology, specific surface area, and the ability to form filler networks. In industrial practice, precipitated silica is commonly used with silane coupling agents, which significantly affect reinforcement efficiency. In the present study, a comparison was performed under identical, non-silanized conditions to evaluate the intrinsic contribution of the mineral phase. Therefore, the observed differences reflect the inherent structural and morphological characteristics of the fillers within the selected formulation.

The tensile strength decreases moderately from 13.54 MPa in the reference compound to 12.98 MPa with 20 phr of zeolite. While zeolite's reinforcing efficiency appears slightly lower than silica's, all compositions remain above the required industrial threshold of 12 MPa. At the same time, elongation at break steadily increases, reaching 433% at the highest zeolite content. This reduction in compound rigidity and enhanced deformability may be advantageous for sealing applications subjected to cyclic loading. This effect may also be related to a more uniform stress distribution within the elastomer matrix due to weaker filler networking. Reduced filler-filler interactions can lead to improved chain mobility and more homogeneous deformation under load, explaining why elongation at break increases without significant loss of tensile strength. Tear resistance shows only a limited reduction and remains significantly above the specified minimum value. Shore A hardness decreases slightly, which is consistent with the observed increase in flexibility. After complex climatic aging, all compositions retain acceptable elongation values, and the change relative to the initial properties remains within the permitted range, suggesting that the incorporation of zeolite does not adversely affect network stability under environmental exposure, as depicted in Figure 4.

TABLE II. FORMULATION OF RUBBER COMPOUNDS FOR THE MANUFACTURE OF HYDRAULIC SEALING ELEMENTS (PHR)

Name of ingredients	**Parts per hundred rubber (phr)**				
	Reference	1	2	3	4
SKI-3 1st group	100	100	100	100	100
Carbon black	4	4	4	4	4
Sulfenamide M	0.8	0.8	0.8	0.8	0.8
Santogard PVJ	0.2	0.2	0.2	0.2	0.2
Zinc oxide	5	5	5	5	5
Stearic acid	2	2	2	2	2
Pine rosin	2	2	2	2	2
Softener ASMG	3	3	3	3	3
Oil PN-6SH	6	6	6	6	6
Protective microwax 3B-1	1	1	1	1	1
Acetonanil R	2	2	2	2	2
Diafen FP	2	2	2	2	2
Precipitated silica	20	15	10	5	0
Zeolite	0	5	10	15	20
Carbon black P - 220	60	60	60	60	60
Total	208	208	208	208	208

TABLE III. RHEOLOGICAL AND MECHANICAL PROPERTIES OF RUBBER COMPOUNDS AND VULCANIZATES

Name of ingredients	**Standard**	**phr**				
		Reference	1	2	3	4
Content of precipitated silica, phr		20	15	10	5	0
Content of zeolite, phr		0	5	10	15	20
Mooney viscosity MV 1+4 (100 °C), conventional units		44	43	43	42	41
Tensile strength, MPa	not less than 12.0	13.54	13.45	13.36	13.21	12.98
Relative elongation at break, %	not less than 350	420	422	425	430	433
Tear resistance, kN/m	not less than 40.0	53.96	53.05	52.52	51.48	50.58
Shore hardness, A, conventional units, not less than	62 ± 5	60	60	59	59	58
Relative elongation at break after complex climatic aging, %	not less than 250	317	323	325	330	335
Change in relative elongation at break after complex climatic aging according to indicators from actual values determined before climatic aging, %	± 30%	-25%	-23%	-24%	-23%	-23%

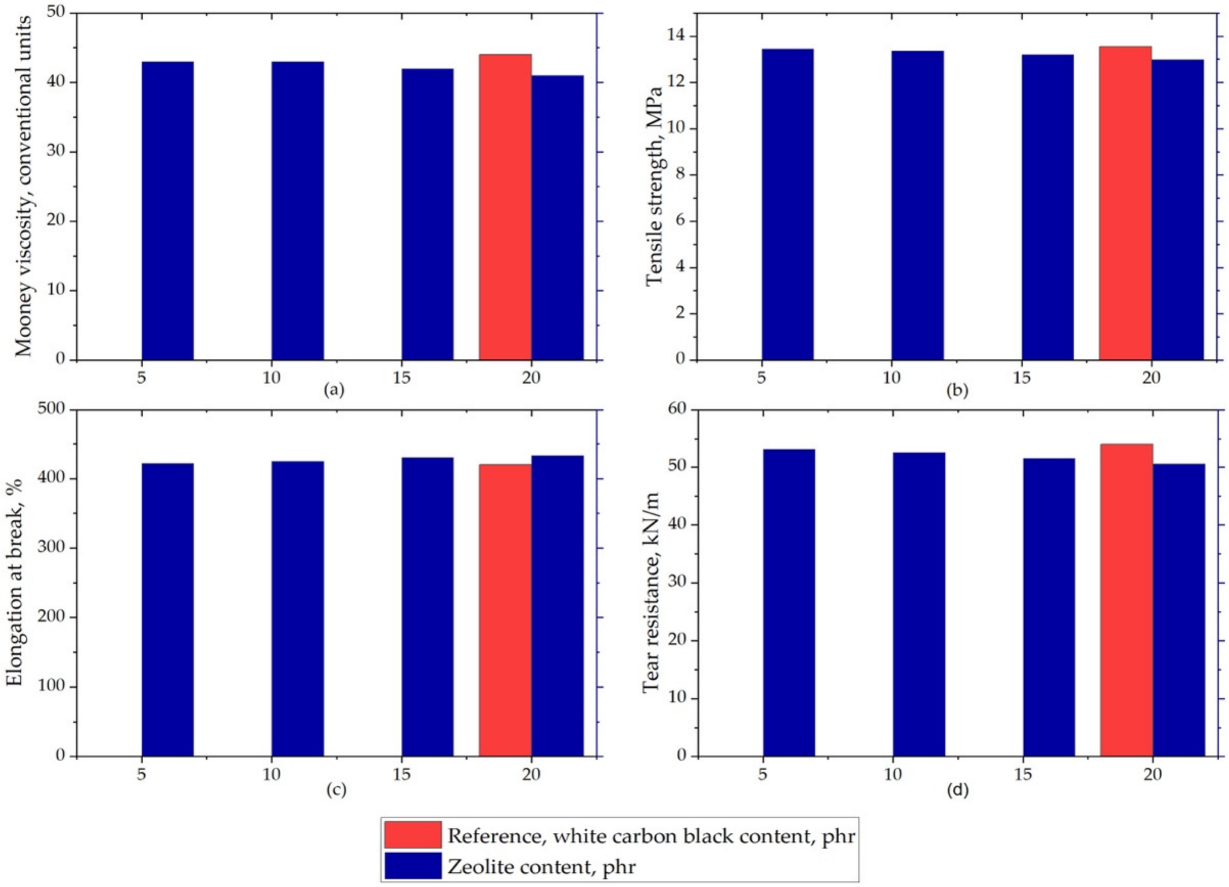

Fig. 4. Influence of zeolite content on: (a) Mooney viscosity, (b) tensile strength, (c) elongation at break, (d) tear resistance.

IV. CONCLUSIONS

This study examined how acid-treated natural zeolite behaves as a partial mineral component in SKI-3-based rubber compounds intended for hydraulic sealing applications. The investigation was conducted under controlled, non-silanized conditions to evaluate the intrinsic contribution of the mineral phase in a defined formulation. Structural analysis revealed that acid activation, followed by thermal treatment, results in minor composition changes while maintaining the aluminosilicate framework's integrity. Morphological observations revealed improved surface uniformity after treatment, which suggests a potential influence on filler dispersion and network formation. Replacing precipitated silica with modified zeolite (5-20 phr) gradually resulted in a slight decrease in Mooney viscosity and a moderate reduction in tensile strength. Conversely, elongation at break increased, and tear resistance and aging stability remained within acceptable performance limits, suggesting a shift in the balance between stiffness and deformability rather than a loss of reinforcement. Overall, the results demonstrate that acid-treated natural zeolite can effectively replace precipitated silica in elastomer compositions for hydraulic sealing applications. Incorporating zeolite improves processability while maintaining the required level of mechanical performance. These findings underscore the potential of natural clinoptilolite as a cost-effective, sustainable mineral filler in industrial rubber formulations.

DECLARATION OF COMPETING INTERESTS

The authors declare no conflict of interest.

ACKNOWLEDGMENT

Not applicable to this work.

DATA AVAILABILITY

The data supporting the findings of this study are available within the article. The authors can provide additional data upon reasonable request.

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