Iranian Journal of Materials Forming 12 (2) (2025) 15-21

Online ISSN: 2383-0042

IJMF

Iranian Journal of Materials Forming

Journal Homepage: http://ijmf.shirazu.ac.ir

Research Article

Mechanical and Thermal Characteristics of Clay-Incorporated Vinyl Ester Composite

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ARTICLE INFO

Article history:

Received 30 January 2025
Reviewed 25 February 2025
Revised 18 March 2025
Accepted 3 April 2025

Keywords:

Vinyl ester
Clay
Composite
Mechanical properties
Thermal properties

Please cite this article as:

Zebarjad, S. M., Setoodeh, A., & Bonyani, M. (2025). Mechanical and thermal characteristics of clay-incorporated vinyl ester composite. *Iranian Journal of Materials Forming*, *12*(2), 15-21. https://doi.org/10.22099/IJMF.2025.52319.1323

ABSTRACT

Vinyl ester (VE) polymer composites reinforced with varying amounts of clay were synthesized using an ultrasonic dispersion technique with the addition of methyl ethyl ketone peroxide (MEKP), cobalt napthalate and benzoyl peroxide as initiators and catalysts. The mechanical and thermal properties of these clay-filled VE composites were systematically evaluated. Mechanical testing—including tensile, flexural, and impact analysis—was conducted using a universal testing machine (UTM) and an Izod impact tester. The incorporation of clay at 0, 5, 10, and 15 wt.% enhanced the tensile strength of the composites to values of 105, 120, and 125 MPa, respectively, compared to 86 MPa for the pristine VE. Similarly, flexural strength increased to 145, 160, and 190 MPa from an initial 125 MPa. In contrast, impact energy remained relatively unchanged with clay addition. Thermal behavior assessed through thermogravimetric analyzer (TGA) revealed that higher clay loadings resulted in increased decomposition temperatures and residual weight. The $T_{50\%}$ analysis reveals that an increase in clay content leads to higher degradation temperatures and as a result, greater residual weight. The $T_{50\%}$ values are 350, 500, 550, and 650 °C for the 0, 5, 10, and 15 wt.% clay composites, respectively. Overall, the inclusion of clay significantly improved both the mechanical and thermal performance of the VE matrix.

1. Introduction

There is a growing interest in polymer-based composites that are reinforced with materials such as clay, carbon nanotubes, silicates, and ceramics to enhance their mechanical, thermal, and electrical performance [1]. Among these, clay is widely used across various industries—including aerospace, cable coating, sports equipment, marine systems, and automotive manufacturing—owing to its lightweight nature, favorable strength-to-weight ratio, and ease of processing [2]. When dispersed within an engineering polymer matrix, layered silicates act as a key

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https://doi.org/10.22099/IJMF.2025.52319.1323

reinforcement phase, forming an important class of organic–inorganic hybrid composites [3]. Gabr et al. [4] investigated the influence of organoclay on the mechanical and thermal characteristics of woven carbon fiber/polypropylene composites with compatibilizers. The study revealed that incorporating 3% organoclay increased the glass transition temperature by about 6 °C compared to the unmodified composite, suggesting improved thermal resistance. Similarly, Essabir et al. [5] explored a hybrid composite composed of oil-palm fiber (OPF) and clay, reinforced within a high-density polyethylene (HDPE) matrix using twin-screw extrusion followed by injection molding. The composite with a 12.5:12.5 weight ratio of OPF to clay demonstrated a 49% increase in Young's modulus and an 11% improvement in tensile strength. The presence of clay also contributed to enhanced thermal stability when compared to composites made solely from OPF.

The final processing of such composites is influenced by multiple processing variables [6]. A widely recognized factor in improving the performance of clay-based composite is the effective exfoliation of silicate layers within the polymer matrix [7–9]. However, achieving full exfoliation through current processing techniques remains technically demanding. Techniques such as ultrasonication can assist in exfoliating silicate layers suspended in water or organic solvents. Additionally, high-energy ball milling of solid silicates may promote partial exfoliation. The main processing approaches for fabricating clay/polymer composites include in situ exfoliation, solution intercalation/exfoliation, and melt intercalation methods [8, 10, 11].

This study investigates the effect of incorporating clay into vinyl ester (VE) on its mechanical and thermal properties. Although prior research has explored the individual characteristics of VE and clay, comprehensive studies examining their combined performance remain limited.

For this purpose, a high-energy ball mill was employed to exfoliate the clay. VE resins are widely used in polymeric composite applications due to their excellent chemical resistance, along with strong thermal stability and mechanical performance. Their notable attributes—such as high corrosion resistance, favorable mechanical strength, low shrinkage, long-term durability, and ease of processing—make them highly suitable for demanding industrial applications [12–14].

2. Experimental Procedure

2.1. Materials and methods

VE resin based on a Bisphenol A epoxy backbone (Swancor, 901), was employed as the composite matrix. This resin exhibits a viscosity of 450 cps and a gelation time of 15-20 minutes at air temperature. Styrene, present in the VE resin, functioned as a crosslinking agent. To initiate the crosslinking process, 1 wt.% methyl ethyl ketone peroxide (MEKP) was used, while cobalt catalyst (0.018 wt.%) was added as an accelerator. The clay used in this study was organically modified sodium montmorillonite (Na-MMT), supplied by Nanolyn (China). To exfoliate the silicate layers and reduce clay particle agglomeration, a planetary ball mill machine was utilized at 250 rpm for 10 h at room temperature, employing 10 mm stainless steel balls. The ball-to-powder weight ratio was maintained at 20:1.

Prior to incorporation into the resin, clay particles were suspended in ethanol and subjected to ultrasonication for 45 min using a tip sonicator (Parsonic 2600 S) to enhance dispersion. Clay loadings of 0, 5, 10, and 15 wt.% were added to the VE resin through simultaneous ultrasonication and magnetic stirring for 10 min. Following dispersion, the mixtures were centrifuged at 6000 rpm for 20 min. After centrifugation, the VE-clay suspensions were degassed under vacuum for 20 min to eliminate entrapped air. The resulting mixtures were then cast into silicone molds (in accordance with ASTM D3039 standards) and cured at room temperature for 24 h. Finally, the cured samples were polished with sandpaper, and all edges were carefully smoothed to avoid stress concentrations. The geometry and dimensions of the standard tensile and bending specimens are shown in Fig. 1.

2.2. Morphological study

The surface morphology of the composites was

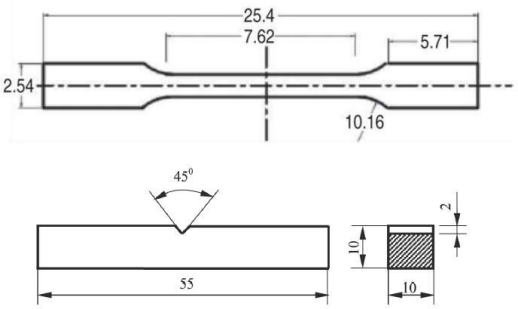

Fig. 1. Shape and dimensions of the standard specimen used for tensile and bending test [15].

examined using a scanning electron microscope (SEM, Hitachi S-4200, Hitachi Limited, Tokyo, Japan) operated at an accelerating voltage of 20 kV.

2.3. Mechanical analysis

2.3.1. Tensile strength testing

Tensile properties were evaluated according to ASTM standard D3039 using Zwick universal testing machine (Model Z250) [16]. A uniaxial load was applied at a constant crosshead speed of 1 mm/min. For each composition, three specimens were tested, and the average tensile strength was reported.

2.3.2. Three-point bending test

Flexural properties were determined through three-point bending tests in accordance with DIN EN ISO 178 [17]. Three specimens from each group were tested at two different crosshead speeds: 10 mm/min and 30 mm/min. This approach enabled the calculation of mean values and standard deviations for both flexural modulus and flexural strength.

2.3.3. Impact testing

Low-velocity impact resistance was assessed using an instrumented drop-weight impact tester (Instron Model 8250), following ASTM D256 standard [18]. Specimens with dimensions of 127 mm × 12.7 mm × 6.35 mm were impacted at a velocity of 3.5 m/s under ambient conditions.

2.3.4. Dimensional stability

The thermal dimensional stability of the composites was evaluated using a DIL 2010STD dilatometer (Orton, USA). The setup consisted of a furnace, fused quartz probe rod, LVDT sensors, thermocouples, and a precision sample holder. Specimens measured 150 mm in length and 4 mm in width. Each sample was subjected to a thermal cycle from room temperature up to 200 °C at a controlled heating rate of 10 °C/min.

2.4. Thermal analysis

Thermogravimetric analysis (TGA) was performed using a Du Pont TGA 2900 analyzer. The samples were heated from 30 to 700 °C at a rate of 10 °C/min under a nitrogen (N_2) atmosphere to assess their thermal stability.

3. Results and Discussion

3.1. Tensile strength testing

Fig. 2 presents the stress-strain behavior of VE composite with varying clay content. The incorporation of clay into the VE matrix resulted in a marked improvement in both tensile strength and elastic modulus (Table 1). Specifically, composites with 5, 10, and 15 wt.% clay exhibited tensile strengths of 105, 120 and 125 MPa, respectively—significantly higher than that of VE resin. This enhancement in tensile strength is primarily attributed to the homogeneous dispersion of clay within the matrix and the strong interfacial interaction between the clay particles and the polymer chains. The presence of alkyl ammonium ions in the organically modified clay promotes adhesion, thereby facilitating effective stress transfer throughout the composite structure [19].

Table 1. Tensile properties of VE/clay composites as a function of clay content

Property	VE/clay			VE
	5 wt.% clay	10 wt.% clay	15 wt.% clay	
Young's modulus (MPa)	3.1±0.1	3.85±0.1	4.1±0.1	2.95±0.1
Tensile strength (MPa)	105±4.2	120±4.8	125±5	86±3.4
Elongation (%)	3.8±0.1	3.1±0.1	2.8±0.1	6.1±0.2

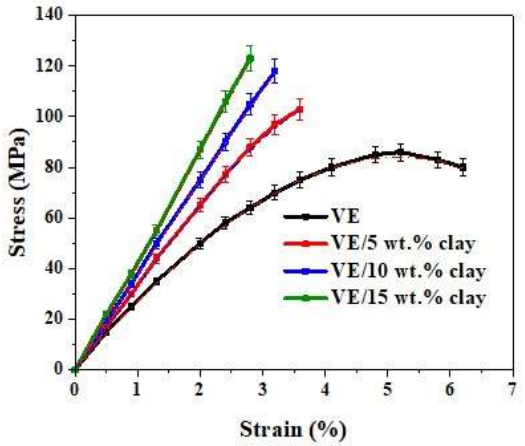

Fig. 2. Stress-strain curves of VE/clay composites with varying clay content.

The enhancement in elastic modulus is due to the exfoliation and effective dispersion of clay particles, which limit the movement of polymer chains, along with the strong adhesion between the clay and VE matrix. Additionally, the VE elongation decreases as the amount of clay increases.

Fig. 3 presents the fracture surface morphology of both pristine VE and the VE/clay (5 wt.%) composite following tensile testing. The composite containing clay exhibits noticeably different fracture features compared to the unreinforced VE. Additionally, the clay appears to be well-dispersed throughout the polymer matrix, with an average particle size ranging from 500 nm to 1 µm. The improvement in the strength of the composite is attributed to a crack-deflection mechanism and the physical locking effect introduced by the dispersed clay platelets, which collectively hinder crack propagation and improve load-bearing capacity.

3.2. Flexural behavior

The variation in flexural stress for VE/clay composites is exhibited in Fig. 4. The incorporation of clay into the polymer matrix significantly influences its flexural properties. Table 2 presents the flexural modulus of VE resin increased by approximately 2.7, 3.2, and 3.8 MPa with the addition of 5, 10, and 15 wt.% clay, respectively. The addition of clay influences the interfacial characteristics of the composites, such as the adhesive strength and interfacial stiffness of the composite material [20].

These interfacial characteristics are critical for efficient stress transfer and elastic deformation during mechanical loading. The uniform dispersion of clay throughout the matrix enhances the effective surface area in contact with the polymer, resulting in improved interfacial bonding. Consequently, this promotes more efficient load transfer, leading to an overall increase in flexural stiffness. Moreover, the flexural strength of the VE/clay composites increased progressively, reaching values up to 190 MPa. It is worth noting that the distribution of clay particles within the matrix plays a crucial role in determining the overall mechanical performance.

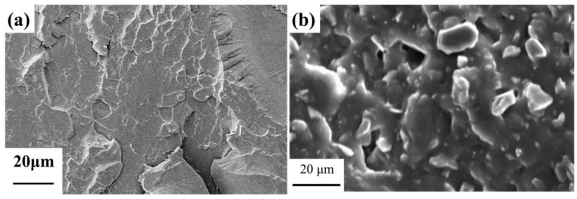

Fig. 3. Fracture surfaces of (a) pristine VE and (b) VE composite containing 5 wt.% clay after tensile testing.

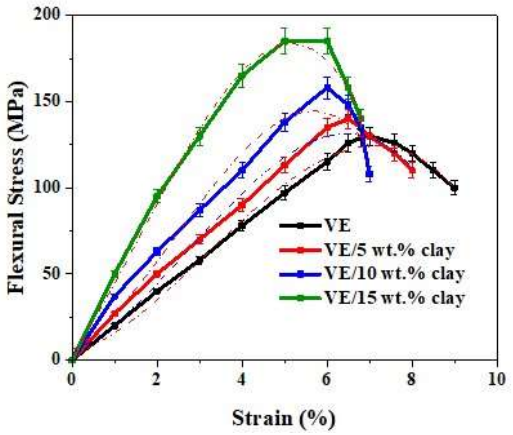

Fig. 4. Flexural stress-strain curves of VE/clay composites with varying clay content.

Table 2. Flexural properties of VE/clay composites as a function of clay loading

Property	VE/clay			VE
	5 wt.% clay	10 wt.% clay	15 wt.% clay	
Flexural modulus (MPa)	2.7±0.1	3.2±0.1	3.8±0.1	2±0.08
Flexural strength (MPa)	145±5.8	160±6.4	190±7.6	125±5

3.3. Impact analysis

The impact results of the VE/clay composite are illustrated in Fig. 5. Despite the increase in clay content, which made the matrix more brittle while improving its strength, there was no significant change in impact resistance. However, as the concentration of clay increases, the impact energy tends to decrease due to the formation of clay aggregates.

3.4. Dimensional stability

Fig. 6 illustrates the dimensional variations of VE/clay composites after being subjected to elevated temperatures and cooled to room temperature. The incorporation of clay significantly influences the dimensional stability of VE matrix. In particular, as the clay content increases, the extent of dimensional change at 200 °C decreases.

The decrease in length change values of the composites can be attributed to the lower coefficient of thermal expansion (CTE) of clay compared to the VE matrix (~0.3 × 10^{-3} 1/°C, from 125 to 170 °C), which is influenced by the stiffness of the matrix [21]. The CTE for the VE/clay composite is approximately 0.2 × 10^{-3}, 0.1 × 10^{-3}, and 0.1 × 10^{-3} 1/°C from 125 to 170 °C for clay contents of 5, 10, and 50 wt.%, respectively. These findings clearly indicate that increasing the clay content leads to a marked improvement in thermal dimensional stability by minimizing expansion at elevated temperatures.

3.5. TGA results

The composites containing varying amounts of clay were analyzed using TGA, and the corresponding weight loss with increasing temperature is illustrated in Fig. 7. The VE/clay composite exhibited a slower decomposition rate across a wide temperature range, leading to reduced emission of volatile compounds. This behavior reflects an improvement in thermal stability at elevated temperatures. Although the degradation profiles of the composites were generally similar, a noticeable difference in residual weight was observed. The temperatures corresponding to 50% weight loss (T_{50}%) were approximately 350, 500, 550, and 650 °C for composites containing 0, 5, 10 and 15 wt.% clay, respectively. These results indicate that higher clay content leads to increased degradation temperatures and greater thermal residue. A slightly lower degradation rate was noted for the 15 wt.% clay composite, suggesting that increasing clay content can significantly affect the thermal degradation behavior. The presence of clay between the crosslinked chains likely impedes thermal decomposition, contributing to the observed reduction in degradation rate as clay content increases [22].

The addition of clay significantly enhances the tensile and flexural properties of VE composite; however, this reinforcement often involves trade-offs, including increased brittleness and reduced ductility. While clay contributes to improved strength, it may

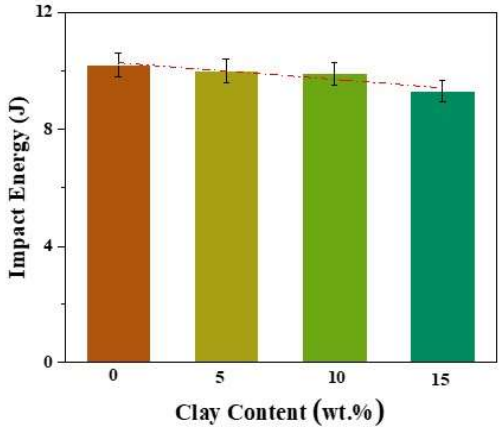

Fig. 5. Comparison of impact energy for VE/clay composites with varying clay content.

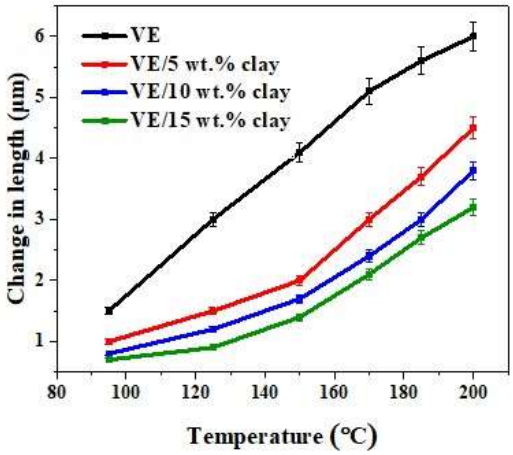

Fig. 6. Temperature-dependent dimensional of VE/clay composites with varying clay content.

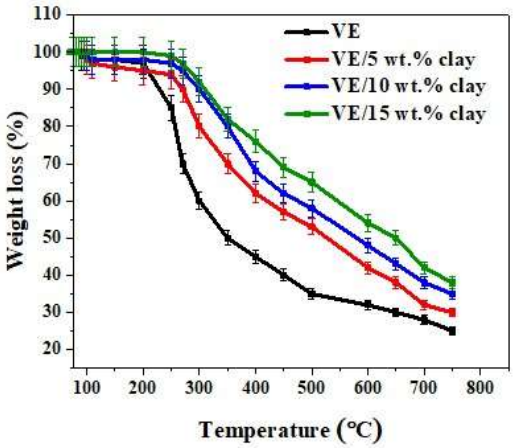

Fig. 7. TGA curves of VE/clay composites with varying clay contents.

compromise the material's capacity to absorb energy prior to failure. Hence, a balanced approach is necessary to optimize mechanical performance without sacrificing overall toughness.

4. Conclusions

This study systematically investigated the mechanical and thermal behavior of VE composites reinforced with varying amounts of clay. The key findings are as follows:

1. The incorporation of clay into VE markedly improved its tensile strength and elastic modulus, with the composite demonstrating tensile strengths of 105, 120, and 125 MPa at 5, 10, and 15 wt.% of clay, respectively, which exceed the tensile strength of pristine VE.
2. Flexural properties were also positively influenced by clay addition. The flexural modulus increased by approximately 2.7, 3.2, and 3.8 MPa for clay contents of 5, 10, and 15 wt.%, respectively.
3. Impact testing demonstrated that although strength increased with higher clay content, the composites exhibited more brittle behavior. Notably, no significant improvement in impact resistance was observed.
4. TGA confirmed improved thermal stability in the VE/clay composites, with higher clay concentrations delaying thermal degradation.
5. Dimensional stability was notably affected by the addition of clay, attributed to differences in the coefficients of thermal expansion between the VE matrix and the clay reinforcement.

Conflict of interest

The authors declare no conflicts of interest related to this study.

Funding

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for profit sectors.

Authors' contributions

S. M. Zebarjad: Data curation, Formal analysis, Investigation, Project administration, Supervision, Validation

A. Setoodeh: Investigation, Supervision, Resources, Validation

M. Bonyani: Conceptualization, Methodology, Writing - original draft, Writing - review & editing.

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