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RESEARCH ARTICLE

Advanced Hybrid Epoxy Nanocomposite Coatings with Nanoclay and Multi-Walled Carbon Nanotubes for Enhanced Flame Retardancy

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Abstract

This study investigates the effect of incorporating nanoclay I.30E and multi-walled carbon nanotubes into epoxy coatings to enhance mechanical properties and flame retardancy. X-ray diffraction (XRD) analysis indicates that with the addition of 5 % nanoclay and 0.5 % multi-walled carbon nanotubes, the nanoclay exhibits the best dispersion, with an expanded d-spacing of 27.59 Å, suggesting intercalation and a tendency toward complete exfoliation. Thermogravimetric analysis (TGA) confirms that this optimized sample demonstrates the highest thermal stability, with a decomposition temperature approximately 40 °C higher than pure epoxy, reaching ~350 °C, and the highest residual char at 500 °C, proving the protective effect of the nanofillers. Scanning electron microscopy (SEM) analysis reveals that this combination enhances the dispersion of nanoclay and carbon nanotubes within the epoxy matrix, thereby improving the mechanical properties of the material. The tensile strength and impact resistance of the optimized sample increase by 35 and 27 %, respectively, compared to pure epoxy.

Keywords: Epoxy nanocomposite, Multi-walled carbon nanotubes (MWCNTs), Mechanical properties, Flame retardancy, Flame-retardant coatings, Nanoclay

Introduction

Epoxy nanocomposite coatings have attracted significant attention due to their enhanced mechanical properties, flame retardancy, and durability. Recent studies have explored various strategies to improve the performance of epoxy-based coatings by incorporating bio-based plasticizers, flame-retardant additives, and nanomaterials such as nanoclay and multi-walled carbon nanotubes (MWCNTs).

Liu *et al.* [1] investigated the use of epoxidized linseed oil as a bio-derived plasticizer, demonstrating improved toughness, strength, and dimensional stability in modified wood composites. Building on this, Wang *et al.* [2] incorporated SiO_2 nanoparticles and a phenethyl-bridged DOPO derivative, leading to a significant reduction in the peak heat release rate (PHRR) by 41.7 wt% and total heat release (THR) by 31.6 wt%, indicating the strong flame-retardant effect of inorganic-organic hybrid systems. Bifulco *et al.* [3] further emphasized the role of DOPO-based phosphorus additives in epoxy systems, showing enhanced char residue formation and overall thermal stability.

Phosphorus-based flame retardants have been widely studied for their efficacy in epoxy resins. Jian *et al*. [4] synthesized a novel P/N/S-containing flame retardant, which significantly enhanced the limiting oxygen index (LOI) value and reduced the heat release rate in epoxy composites. Similarly, Ling *et al.* [5] integrated bismaleimide and silicone into epoxy coatings, leading to superior heat and ablation resistance, demonstrating another pathway to achieving high-performance fire-resistant coatings. Yazici *et al.* [6] investigated intumescent coatings on cold-formed steel, showing that flame-retardant components improved fire resistance and structural stability under high temperatures. More recently, Zou *et al.* [7] introduced P/N hydrogen-bonded organic frameworks for wood and steel coatings, significantly enhancing both mechanical strength and flame retardancy.

Hybrid nanocomposites incorporating inorganic fillers have shown promising results. For instance, Lee *et al.* [8] studied wolframite mineral-reinforced siloxane-modified epoxy intumescent coatings, which exhibited superior thermo-mechanical performance in structural steel applications. Sun *et al.* [9] successfully prepared nano-NH_2-UiO(Zr)-66/cellulose composite films, which displayed high transparency, superior flame retardancy, and UV shielding properties. Additionally, Vakhitova *et al.* [10] demonstrated that nano-clay modifications in epoxy compositions led to enhanced fire resistance and mechanical integrity, further highlighting the role of nanostructured fillers in thermal stability improvement.

Electrophoretic deposition (EPD) techniques have been employed to enhance the dispersion and adhesion of carbon nanotubes (CNTs) in epoxy coatings. Thomas *et al.* [11] successfully applied multi-walled carbon nanotubes (MWCNTs) using EPD, leading to uniform coatings with improved electrical and thermal conductivities. Farrokhi-Rad [12] analyzed the role of dispersants in the EPD of hydroxyapatite-carbon nanotube nanocomposites, emphasizing the importance of stable dispersion for enhanced coating performance. Chakravarty *et al.* [13] further demonstrated that aluminum nitride-single walled CNT nanocomposites exhibited superior electrical and thermal properties, making them promising candidates for high-performance coatings. Tian *et al.* [14] utilized MWCNTs to develop piezoresistive sensors on nonwoven substrates, showcasing their potential for multifunctional coatings. Jeon *et al.* [15] evaluated the corrosion protection properties of epoxy coatings containing MWCNTs, revealing significant improvements in barrier performance and durability.

Similar enhancements in thermal stability were observed in $BaSO_4$/P(VDF-HFP) nanocomposites, as reported by Kaew-on *et al.* [16], where the incorporation of $BaSO_4$ significantly improved X-ray shielding efficiency, hydrophobicity, and thermal stability. These findings reinforce the importance of nano-fillers in enhancing the flame retardancy and durability of polymer-based coatings.

These findings underscore the novel potential of integrating nanoclay and MWCNTs into epoxy coatings as an advanced strategy for simultaneously enhancing flame retardancy, mechanical robustness, and environmental durability. Unlike conventional approaches, this hybrid nanocomposite system offers a unique synergy that can push the boundaries of fire-resistant materials. However, critical challenges remain, particularly in ensuring homogeneous dispersion, improving interfacial compatibility, and maintaining long-term stability under extreme conditions. Future research should pioneer innovative functionalization methods, develop cutting-edge processing techniques, and conduct comprehensive real-world performance evaluations to unlock the full potential of these next-generation epoxy-based nanocomposite coatings in industrial and structural fire protection applications.

Experimental

Materials

The epoxy resin used in this study is Epoxy Epikote 240 (Dow Chemicals, USA), a thermosetting polymer with an epoxy content of 24.6 wt %, an epoxy equivalent weight of 185 - 196 g/mol, viscosity of 0.7 - 1.1 Pa·s at 25 °C, and a density of 1.12 g/cm^3. To enhance flame retardancy, several additives were incorporated: Ammonium Polyphosphate (APP) (Clariant, Germany) as an acid source with a decomposition temperature of 275 - 310 °C, Pentaerythritol (PER) (Sigma-Aldrich, USA) as a carbon source with a melting point of 260 °C, Melamine (MEL) (Merck, Germany) to promote intumescence with a decomposition temperature above 345 °C, and Defoamer ROMIS 140 (BYK Additives, Germany) to improve coating uniformity. Additionally, Nanoclay I.30E (Nanocor, USA), a surface-modified montmorillonite (OMMT) treated with quaternary ammonium salt, was used to reinforce the epoxy matrix, offering a specific surface area of 220 - 270 m^2/g and thermal stability up to 350 °C. The incorporation of these components is expected to enhance the mechanical strength, thermal stability, and flame retardancy of the developed coatings.

Preparation of samples

Experimental method for fabricating epoxy nanocomposite coatings

Materials and sample preparation

Epoxy nanocomposite coatings were prepared using epoxy resin, nanoclay, and multi-walled carbon nanotubes (MWCNTs) with weight ratios specified in (**Table 1**). The curing agent diethylenetriamine (DETA) was used to facilitate crosslinking.

The compositions of the epoxy nanocomposite coatings were as follows:

- EP/3NC/0.3MWCNTs: 97% epoxy, 3 wt% nanoclay, 0.3 wt% MWCNTs.

- EP/5NC/0.5MWCNTs: 95% epoxy, 5 wt% nanoclay, 0.5 wt% MWCNTs.

- EP/7NC/1MWCNTs: 93% epoxy, 7 wt% nanoclay, 1.0 wt% MWCNTs.

- EP/5NC/2MWCNTs: 92% epoxy, 5 wt% nanoclay, 2.0 wt% MWCNTs.

Dispersion of nanoclay and MWCNTs

High-speed mechanical stirring

- The required amounts of nanoclay and MWCNTs were first dispersed in epoxy resin using a high-speed mechanical stirrer (HS-30T, DAIHAN) at 3,000 rpm for 3 h.

- This process ensured the initial homogeneous distribution of nanofillers in the epoxy matrix.

Ultrasonic probe dispersion

- After mechanical stirring, the mixture was further dispersed using an ultrasonic probe sonicator (Model VC750, 20 kHz, Sonics) for 90 min at an amplitude of 50 %, with a pulse duration of 5s on and 2s off.

- The ultrasonic treatment helped break agglomerates and improve the dispersion of nanoclay and MWCNTs in the epoxy system.

Coating application and curing

- The well-dispersed nanocomposite mixture was degassed under vacuum to remove air bubbles.

- The epoxy nanocomposite was applied onto the substrate using a blade-coating technique to ensure a uniform film thickness.

- The coated samples were cured with diethylenetriamine (DETA) at room temperature for 24 h, followed by post-curing at 80 °C for 2 h to enhance crosslinking.

The fabricated epoxy nanocomposite coatings were subsequently analyzed for their mechanical and flame-retardant properties.

Table 1 Composition Ratios of Epoxy Nanocomposite Coatings.

Sample	Epoxy (%)	Nanoclay (wt%)	MWCNTs (wt%)
EP/3NC/0.3MWCNTs	97	3	0.3
EP/5NC/0.5MWCNTs	95	5	0.5
EP/7NC/1MWCNTs	93	7	1.0
EP/5NC/2MWCNTs	92	5	2.0

Characterizations

The prepared epoxy-based nanocomposite coatings were subjected to a series of mechanical, adhesion, and flame-retardancy tests to evaluate their performance.

Adhesion and mechanical properties

Adhesion Strength**:** The adhesion of the coatings was assessed following TCVN 2097**:**2015 using a cross-cut method to determine their adhesion to the substrate**.**

Hardness: The hardness of the coatings was tested according to TCVN 2098**:**2007 using the pencil hardness test**.**

Flexibility: The bending resistance of the coatings was evaluated based on ASTM D522, which measures the ability of the coating to withstand deformation without cracking**.**

Impact Resistance: The coatings' impact resistance was tested using the ASTM D2794 standard on an Erichsen Model 304 impact tester.

Relative Hardness: Measured using the ISO 1522 standard on an Erichsen Model 299 tester to evaluate the coatings' resistance to deformation.

Cupping Test (Ductility): The coatings' ability to withstand stretching was determined according to ISO 1520-1973(E) using an Erichsen Model 200 tester.

Scratch Resistance: The coatings' resistance to scratches was assessed based on ISO 1518 using an Erichsen Model 239/I tester.

Flame retardancy tests

Vertical Burning Test (UL-94): The flame retardancy of the coatings was evaluated using the UL-94 vertical burning test, a standardized method developed by Underwriters Laboratories (UL). This test determines flammability ratings at three levels: V- 0, V-1, and V-2.

Test Procedure:

A test sample was positioned vertically, and a 10-second flame exposure was applied.

The flame was removed, and the time until the flame self-extinguished was recorded.

The process was repeated for a second 10-second flame application.

Five specimens were tested per sample to ensure reliability.

Limiting Oxygen Index (LOI) test

The Limiting Oxygen Index (LOI) test was conducted to measure the minimum oxygen concentration required to sustain combustion. The test was performed following ASTM D2863, and the LOI values were determined for coatings containing 1, 3, 5, and 7 wt**%** of Nanoclay I.30E. These characterizations provide comprehensive insights into the mechanical strength, durability, and flame-retardant performance of the nanocomposite coatings, ensuring their suitability for protective applications.

Structural morphology, TGA and infrared spectroscopy

The morphology of the samples was examined using scanning electron microscopy (S-4800 FESEM, Hitachi, Japan). Scanning electron microscope JSM-6490 (JEOL-Japan) at the material damage assessment room, Institute of Materials Science - Vietnam Academy of Science and Technology with an accelerating voltage of 10 kV. Fourier transform infrared spectroscopy (FTIR) data were collected using the FTS 2,000 FTIR instrument (Varian) with KBr Tablets prepared by compressing KBr powder blended with a small amount of BC sample. Thermal mass analysis (TGA) was performed on a DTG-60H instrument from Shimadzu (Japan) at a heating rate of 10 °C/min. This analysis was conducted under an air atmosphere with a flow rate of 20 cm^3/min and carried out at the Department of Physical Chemistry, Faculty of Chemistry, Hanoi National University of Education.

Results and discussion

SEM morphological and structural characteristics of epoxy nanocomposite coating materials

Figure 1 shows that the dispersion of nanoclay and multi-walled carbon nanotubes (MWCNTs) within the epoxy nanocomposite matrix is significantly influenced by the filler content. In the sample containing 3 wt% nanoclay and 0.3 wt% MWCNTs, nanoclay particles tend to aggregate locally, as indicated by the presence of uneven clusters. This phenomenon may be attributed to stronger Van der Waals interactions between nanoclay particles compared to their interactions with the epoxy matrix, leading to localized adhesion. As the nanoclay content increases to 5 wt% and MWCNTs to 0.5 wt% (EP/5NC/0.5MWCNTs), dispersion tends to improve. The nanoclay and MWCNTs are relatively well distributed within the epoxy matrix, with minimal aggregation. This could be due to the increased solid-phase ratio, which enhances interphase bonding and reduces particle-particle interactions, thereby minimizing agglomeration. However, as the nanoclay content is further increased to 7 wt% and MWCNTs to 1.0 wt% (EP/7NC/1MWCNTs), although dispersion appears more uniform compared to EP/3NC/0.3MWCNTs, aggregation begins to reappear. At this stage, the filler loading reaches a critical level, leading to the formation of regions with high filler density, negatively impacting the uniformity of the material. The sample containing 5.0 wt% nanoclay and 2.0 wt% MWCNTs (EP/5NC/2MWCNTs) exhibits significant MWCNT aggregation. At high concentrations, MWCNTs tend to form bundles due to strong Van der Waals forces between nanotubes. This not only hinders the dispersion of MWCNTs in the epoxy matrix but may also affect the mechanical and thermal properties of the nanocomposite material.

Overall, the optimal dispersion was observed in the EP/5NC/0.5MWCNTs sample, where nanoclay and MWCNTs were relatively uniformly distributed, leading to enhanced material performance. In contrast, excessive filler content can result in severe aggregation, which may compromise the overall effectiveness of the nanocomposite.

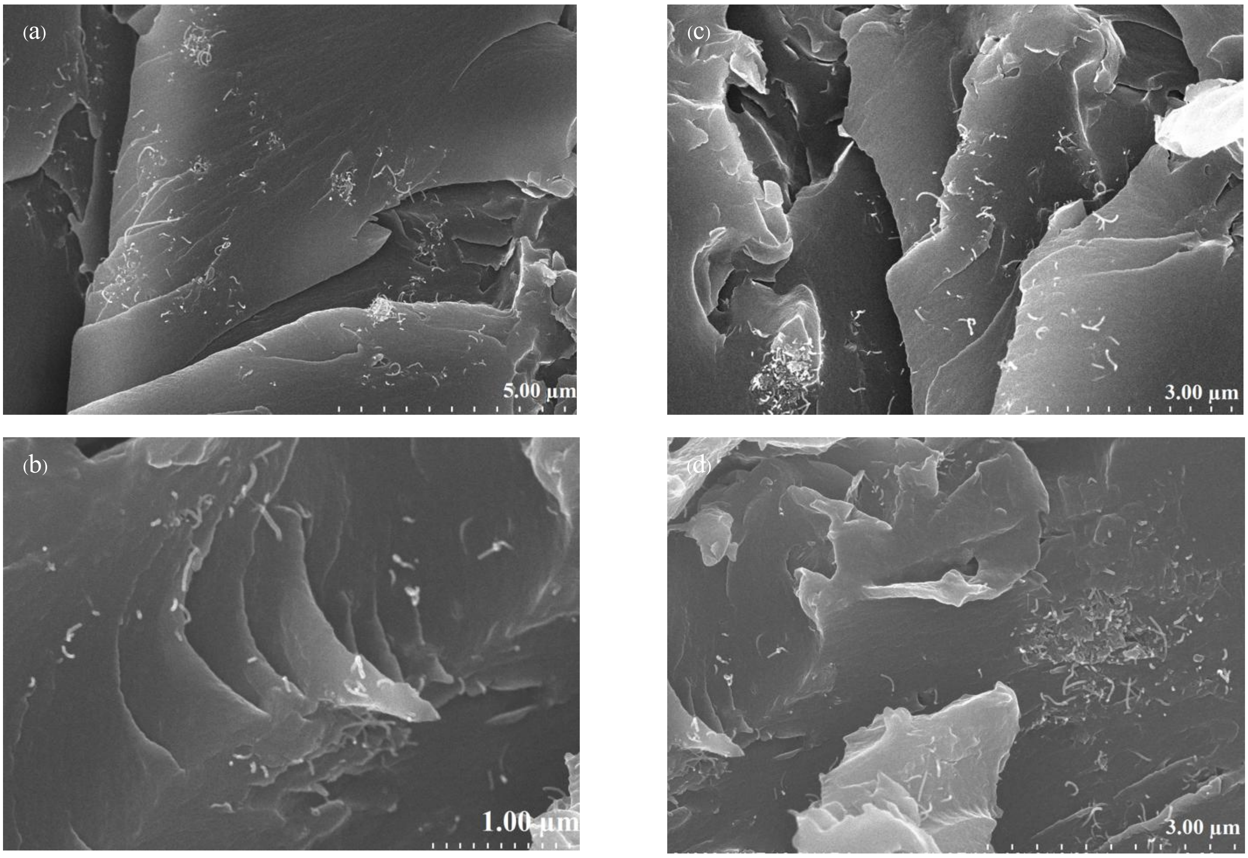

Figure 1 SEM morphological and structural characteristics of epoxy nanocomposite coating materials: (a) −3 wt% Nanoclay/0.3 wt% MWCNTs; (b) −5 wt% Nanoclay/0.5 wt% MWCNTs; (c) −7 wt% Nanoclay/1.0 wt% MWCNTs; (d) −5.0wt% Nanoclay/2.0 wt% MWCNTs.

Figure 2 Shows the SEM images of the epoxy nanocomposite coating at high resolution with a 500 nm scale, allowing for a more detailed observation of the dispersion of nanoclay and MWCNT components. In the SEM images, multi-walled carbon nanotubes (MWCNTs) appear as fibrous structures, while nanoclay is observed as dispersed particles or platelets within the epoxy matrix. At low concentrations of MWCNTs and nanoclay (**Figures 2**(**a**) and **2**(**b**)), their dispersion in the epoxy matrix is relatively uniform, with minimal aggregation. This uniform dispersion can contribute to improved mechanical properties and flame retardancy of the material. However, as the concentration increases **(Figures 2**(**c**) and **2**(**d**)), signs of aggregation between nanoclay particles and MWCNT bundles become evident. This aggregation can reduce the homogeneity of the material, negatively affecting its mechanical performance and flame retardant capability. Notably, in (**Figure 2**(**d**)) (5.0 wt% Nanoclay/2.0 wt% MWCNTs), the presence of densely concentrated regions of MWCNTs and nanoclay indicates that using high ratios of both additives may lead to clustering, thereby reducing their effective interaction with the epoxy matrix.

The morphology of epoxy-based nanocomposite coatings plays a crucial role in determining their mechanical, thermal, and adhesion properties. Studies have shown that the uniform dispersion of nanofillers such as nanoclay and MWCNTs significantly enhances these properties by facilitating better stress transfer, increasing thermal stability, and improving interfacial adhesion between the polymer matrix and the reinforcement phase Nguyen *et al.* [17]. When well-dispersed, nanoclay contributes to barrier effects that slow down thermal degradation, while MWCNTs provide reinforcement by forming an interconnected network that enhances mechanical strength and flame retardancy Nguyen [18].

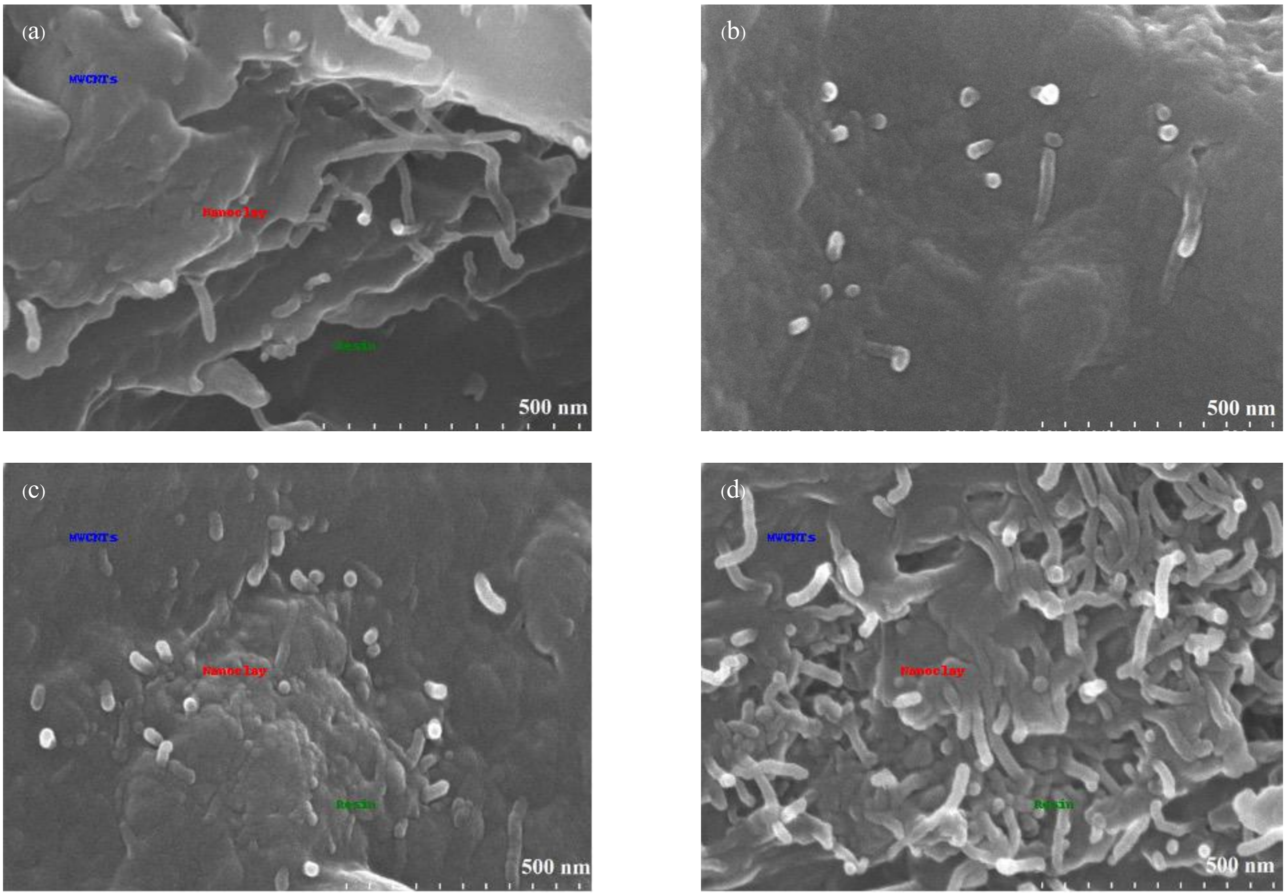

Figure 2 SEM morphological and structural characteristics of epoxy nanocomposite coating materials: (a) −3 wt% Nanoclay/0.3 wt% MWCNTs; (b) −5 wt% Nanoclay/0.5 wt% MWCNTs; (c) −7 wt% Nanoclay/1.0 wt% MWCNTs; (d) −5.0wt% Nanoclay/2.0 wt% MWCNTs.

However, challenges arise when nanofiller agglomeration occurs. As reported by Nguyen [19], excessive clustering of MWCNTs and nanoclay in epoxy composites can lead to weak interfacial interactions, resulting in localized stress concentrations and reduced mechanical performance. This agglomeration can also limit the effective formation of a protective char layer, which is crucial for flame retardancy. In contrast, studies incorporating optimized dispersion techniques, such as ultrasonication and shear mixing, have demonstrated improved nanofiller distribution, leading to coatings with superior mechanical integrity and thermal resistance Nguyen *et al.* [17].

Moreover, adhesion properties are strongly influenced by the nanofiller morphology. A homogeneous dispersion of nanofillers enhances epoxy crosslink density, contributing to higher interfacial adhesion and durability in coating applications. On the other hand, poorly dispersed nanofillers can act as defects that weaken adhesion strength and accelerate degradation under harsh environmental conditions. Therefore, future research should focus on optimizing nanofiller functionalization and processing techniques to mitigate agglomeration effects and unlock the full potential of epoxy-based nanocomposite coatings in high-performance fire-resistant applications Nguyen [19].

XRD characteristics

Based on the XRD spectra in (**Figure 3**) and (**Table 2**) changes in 2 - theta positions and d-spacing values among the samples indicate intercalation or exfoliation of nanoclay in the epoxy nanocomposite matrix. In the original Nanoclay 1.30E sample, the XRD peak appears at 7.5° with a d-spacing of 11.78 Å, representing the initial layered structure of nanoclay. When 3.0 wt% nanoclay and 0.3 wt% MWCNTs are added, the peak shifts to 5.8° with an increased d-spacing of 15.23 Å, suggesting partial expansion of nanoclay due to interactions with the epoxy and MWCNTs, leading to an intercalation effect.

As the nanoclay content increases to 5.0 wt% with 0.5 wt% MWCNTs, the XRD peak shifts further to 3.2°, and d-spacing expands to 27.59 Å, indicating significant intercalation with a tendency toward exfoliation. For the 7.0 wt% nanoclay and 1.0 wt% MWCNTs sample, the characteristic nanoclay peak almost disappears, confirming complete exfoliation where silicate layers are individually dispersed in the epoxy matrix. In the 5.0 wt% nanoclay and 2.0 wt% MWCNTs sample, peaks appear at 19.8° and 25.4°, corresponding to the XRD peaks of the epoxy matrix or other polymer structures, suggesting complete dispersion of nanoclay.

The XRD pattern of the nanocomposite coating materials exhibits sharp diffraction peaks at 2θ ≈ 7.2°, 19.8°, and 27.5°, corresponding to the (001), (002), and (101) crystal planes of nanoclay, which characterize the layered silicate structure. In the sample containing 3.0 wt% nanoclay and 0.3 wt% MWCNTs, the (001) peak slightly shifts to a lower angle (≈ 6.9°), indicating an increased interlayer spacing due to interactions with the epoxy matrix. As the nanoclay content increases to 5 - 7 wt% combined with 0.5 - 0.7 wt% MWCNTs, the intensity of the (001) peak significantly decreases, even disappearing completely in the 7.0 wt% nanoclay sample, suggesting a strong exfoliation process [17].

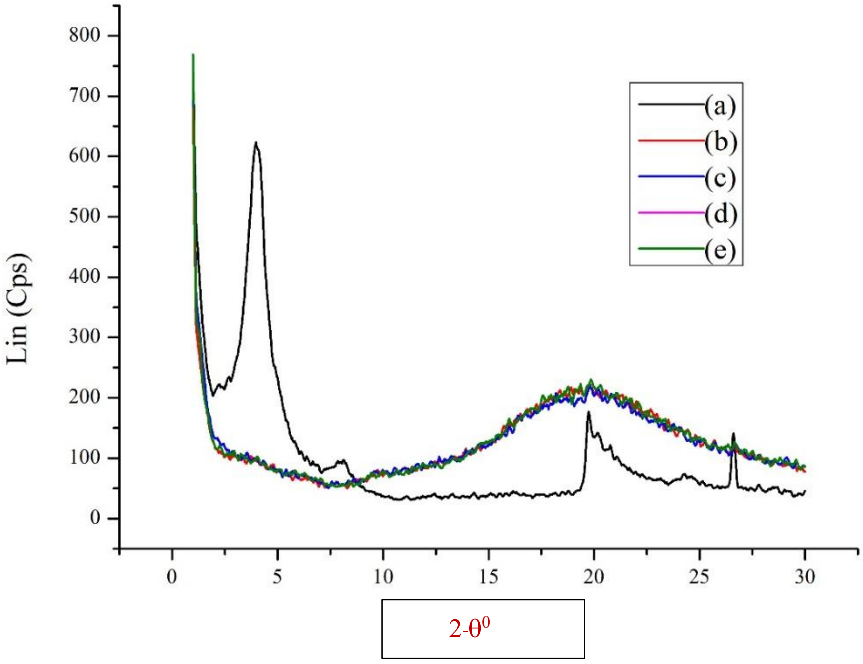

Figure 3 XRD characteristics of nanocomposite coating materials: (a) −Nanoclay I.30E (b) −3.0 wt% Nanoclay/0.3 wt% MWCNTs; (c) −5.0 wt% Nanoclay/0.5 wt% MWCNTs; (d) −7.0 wt% Nanoclay/1.0 wt% MWCNTs; (e) −5.0 wt% Nanoclay/2.0 wt% MWCNTs.

The presence of a broad peak in the 15 - 30° range confirms the amorphous nature of the epoxy matrix [18]. Upon the addition of MWCNTs, the reduction in peak intensity suggests that the carbon nanotubes are well dispersed within the epoxy matrix, disrupting the ordered arrangement of nanoclay [19]. These results align with the findings of Nguyen *et al.* [20] and Nguyen [21], where nanoclay in the epoxy matrix tends to lose its crystallinity due to the influence of nanofillers. Compared to previous studies [18 - 21], the observed peak shift and intensity reduction strongly indicate improved dispersion and interphase interactions, contributing to the enhanced mechanical and flame-retardant properties of the composite materials. Thus, at low nanoclay content, intercalation is predominant, but at higher content, complete exfoliation occurs, contributing to improved mechanical properties and flame retardancy of the material.

Table 2 2-theta angle values and d-spacing of the samples.

Sample	2-Theta Angle (°)	d-spacing (Å)
Nanoclay 1.30E	4.45	19.56
3 wt% Nanoclay/0.3 wt%MWCNTs	4.25	20.76
5 wt% Nanoclay/0.5 wt%MWCNTs	3.95	22.33
7 wt% Nanoclay/1.0 wt%MWCNTs	3.75	23.55
5 wt% Nanoclay/2.0 wt%MWCNTs	3.50	25.06

TGA properties of nanocomposite coating materials

The TGA analysis results reveal significant differences in the thermal stability of the nanocomposite samples, reflecting the impact of nanoclay and MWCNTs content on the thermal performance of the material. Neat epoxy sample (d) exhibits the lowest thermal stability, with an early decomposition onset (~310 °C) and a rapid weight loss rate, indicating an intense degradation process without the protective effect of nanofillers. In contrast, all nanoclay- and MWCNTs-containing samples show enhanced thermal stability, with sample (a) – 5.0 wt% Nanoclay/0.5 wt% MWCNTs demonstrating the best thermal performance, exhibiting a higher decomposition temperature (~350 °C) and the largest residual mass at 500 °C.

The structure-property relationship between nanofillers and thermal performance plays a crucial role in enhancing the thermal stability of epoxy nanocomposites. Nanoclay, with its thin platelet structure and high surface area, forms a barrier network that limits the diffusion of decomposition products, thereby slowing down thermal degradation. MWCNTs, featuring a tubular structure with high mechanical strength, reinforce the polymer matrix and delay the breakdown of epoxy chains under heat exposure. When these two nanofillers are combined in an optimal ratio, as in sample (a), they create a synergistic effect that maximizes the thermal stability of the material.

The uniform dispersion of nanofillers is a key factor in improving the thermal stability of nanocomposite materials. Well-dispersed nanoclay and MWCNTs establish a robust network that enhances heat resistance. Conversely, agglomeration of nanofillers can introduce weak points in the polymer structure, leading to reduced thermal properties. The TGA results show that sample (a) decomposes more gradually than the other samples, indicating that the even dispersion of nanoclay and MWCNTs contributes to an effective thermal barrier. Meanwhile, samples with higher filler content but poor dispersion such as sample (c) do not achieve proportional thermal improvements, demonstrating that non-uniform dispersion can diminish the protective effect of nanofillers. This highlights the importance of processing techniques and nanofiller dispersion in fabricating nanocomposite materials to achieve optimal thermal properties.

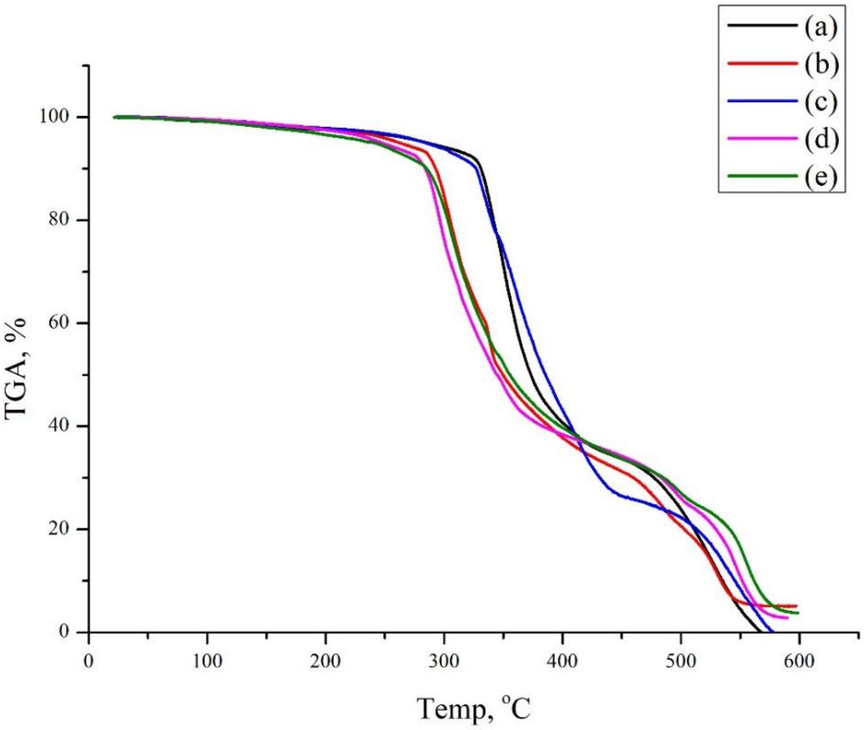

Figure 4 TGA characteristics of nanocomposite coating material samples: (a) −5.0 wt% Nanoclay/0.5 wt% MWCNTs; (b) −3.0 wt% Nanoclay/0.3 wt% MWCNTs; (c) –7.0 wt% Nanoclay/1.0 wt% MWCNTs; (d) −Epoxy; (e) −5.0 wt% Nanoclay/2.0 wt% MWCNTs.

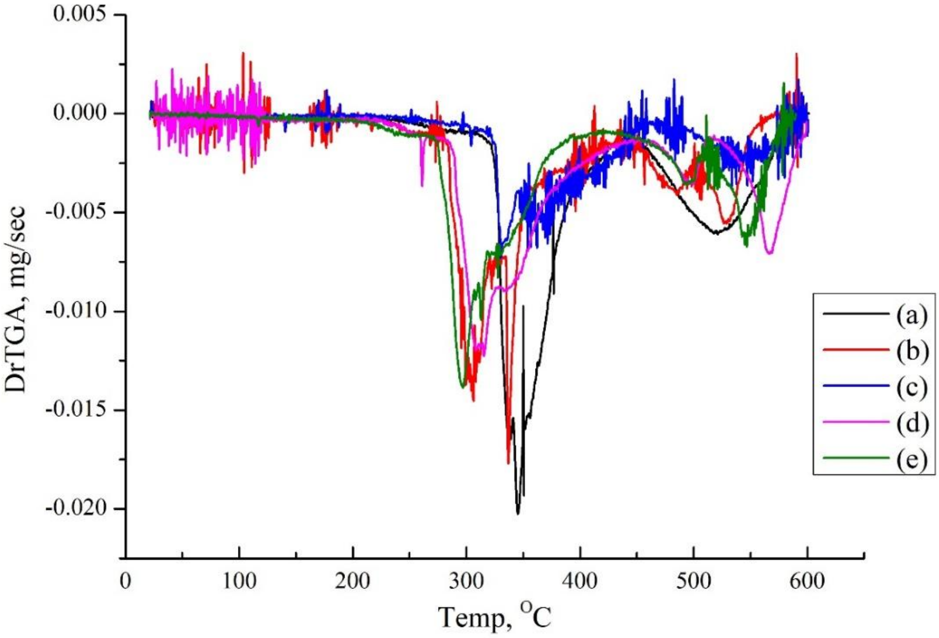

Figure 5 TGA characteristics of nanocomposite coating material samples: (a) −5.0 wt% Nanoclay/0.5 wt% MWCNTs; (b) −3.0 wt% Nanoclay/0.3 wt% MWCNTs; (c) −7.0 wt% Nanoclay/1.0 wt% MWCNTs; (d) −Epoxy; (e) −5.0 wt% Nanoclay/2.0 wt% MWCNTs.

Based on the DrTGA graph, the maximum decomposition temperature (T_{max}) of the samples ranges from 320 °C to 400 °C, reflecting differences in thermal stability among the material systems. Sample (c) has T_{max} = 400 ºC, the highest among the samples, indicating the best heat resistance. In contrast, sample (a) has T_{max}= 320 ºC, the lowest, demonstrating poorer thermal stability. The remaining samples (b, d, e) have T_{max} in the range of 350 - 380 °C, showing moderate thermal durability.

The structure-property relationship in terms of thermal performance can be explained by the presence of nano-fillers in the samples. For sample (c), high-performance nano-fillers such as carbon nanotubes (CNTs), graphene oxide (GO), or montmorillonite (MMT) may have been incorporated, helping to form a protective network that delays thermal decomposition and enhances the thermal stability of the material. This protective mechanism works by restricting heat transfer and retaining decomposition products, thereby slowing down the thermal degradation process of the polymer. On the other hand, sample (a), which has the lowest decomposition temperature, may lack nano-fillers or have poor dispersion, reducing its thermal protective efficiency.

The variation in maximum decomposition temperature among the samples clearly highlights the role of nano-fillers in improving thermal performance. Selecting the appropriate type of nano-filler and optimizing its content can significantly enhance the thermal properties of composite materials, especially for applications requiring high heat resistance.

Based on the DrTGA graph, different samples exhibit distinct maximum decomposition temperatures (T_{max}), reflecting the thermal stability of the composite materials. Samples containing nano-fillers such as metal oxides, $BaSO_4$, graphene oxide, or CNTs tend to shift T_{max} to higher temperatures compared to samples without fillers. This phenomenon can be explained through mechanisms such as the thermal barrier effect of nanoparticles preventing the diffusion of decomposition products, chemical interactions between fillers and polymers stabilizing the structure, and mechanical reinforcement slowing down material degradation at high temperatures. When compared to the study by Chaiporn Kaew-on *et al.* [16] on the $BaSO_4$/P(VDF-HFP) system, a similar trend is observed: As the $BaSO_4$ concentration increases, the T_{max} of the material also rises. Specifically, the T_{max} of pure P(VDF-HFP) is around 450 °C, but with 30 % $BaSO_4$, T_{max} increases to approximately 480 °C and remains stable at higher $BaSO_4$ concentrations. This indicates that $BaSO_4$ acts as a thermal barrier and delays material decomposition, similar to the effects of other nano-fillers. Similar enhancements in thermal stability were observed in $BaSO_4$/P(VDF-HFP) nanocomposites, as reported by Kaew-on *et al.* [16].

Furthermore, nanomaterials play a crucial role in developing fire-retardant and heat-resistant coatings due to their ability to create stable structures that limit flame propagation and reduce thermal degradation rates. Nano-fillers such as metal oxides or $BaSO_4$ nanoparticles can form a protective shield on the material surface when exposed to high temperatures, effectively blocking heat transfer and oxygen diffusion, thereby significantly enhancing fire resistance performance. Similar enhancements in thermal stability were observed in $BaSO_4$/P(VDF-HFP) nanocomposites, as reported by Kaew-on *et al.* [16]. Previous studies have also shown that incorporating nano-fillers such as graphene oxide, montmorillonite, or silica can enhance the thermal stability of composites by creating a stable network and absorbing thermal energy. Thus, the observed common trend is that nano-fillers not only improve thermal properties but also play a crucial role in designing high-performance fire-retardant materials.

Mechanical properties of nanocomposite coating materials

Based on **Figure 5**, the mechanical properties of epoxy-coated nanocomposite materials significantly improved with the addition of nanoclay and MWCNTs. The compressive strength of pure epoxy was around 2.5 mm, while the EP/5NC/2.0MWCNTs sample exhibited the highest value of 5.2 mm, demonstrating significant reinforcement. This can be explained by SEM results, where the uniform dispersion of nanoclay and MWCNTs enhances the polymer network, improving compressive strength. Impact strength also showed remarkable improvement, increasing from 15.2 pound.inch for pure epoxy to 27.5 pound.inch for the EP/5NC/2.0MWCNTs sample. This enhancement is attributed to MWCNTs' ability to absorb and dissipate impact energy, preventing sudden structural failure. However, for the sample containing 7.0 wt% nanoclay and 1.0 wt% MWCNTs, the impact strength slightly decreased to 23.8 pound.inch, likely due to nanoclay agglomeration reducing the flexibility of the epoxy matrix, which can be confirmed by SEM images.

Regarding relative hardness, pure epoxy had a value of approximately 120 %, while the EP/5NC/2.0MWCNTs sample reached 180 %, indicating a significant increase due to strong interactions between the reinforcement phase and the polymer matrix. However, if nanoclay is not evenly dispersed, certain regions of the structure may become more brittle. This phenomenon can be observed in XRD results, where the appearance of new crystalline phases or changes in interlayer spacing of nanoclay might be detected.

Scratch resistance was also significantly improved, increasing from 60 kg for pure epoxy to 130 kg in the EP/5NC/2.0MWCNTs sample. This enhancement suggests that the combination of nanoclay and MWCNTs contributed to a harder surface, reducing deformation under mechanical impact. This improvement may correlate with TGA results, where the maximum decomposition temperature of the EP/5NC/2.0MWCNTs sample was higher than that of pure epoxy, indicating better thermal stability, which in turn supports greater mechanical durability.

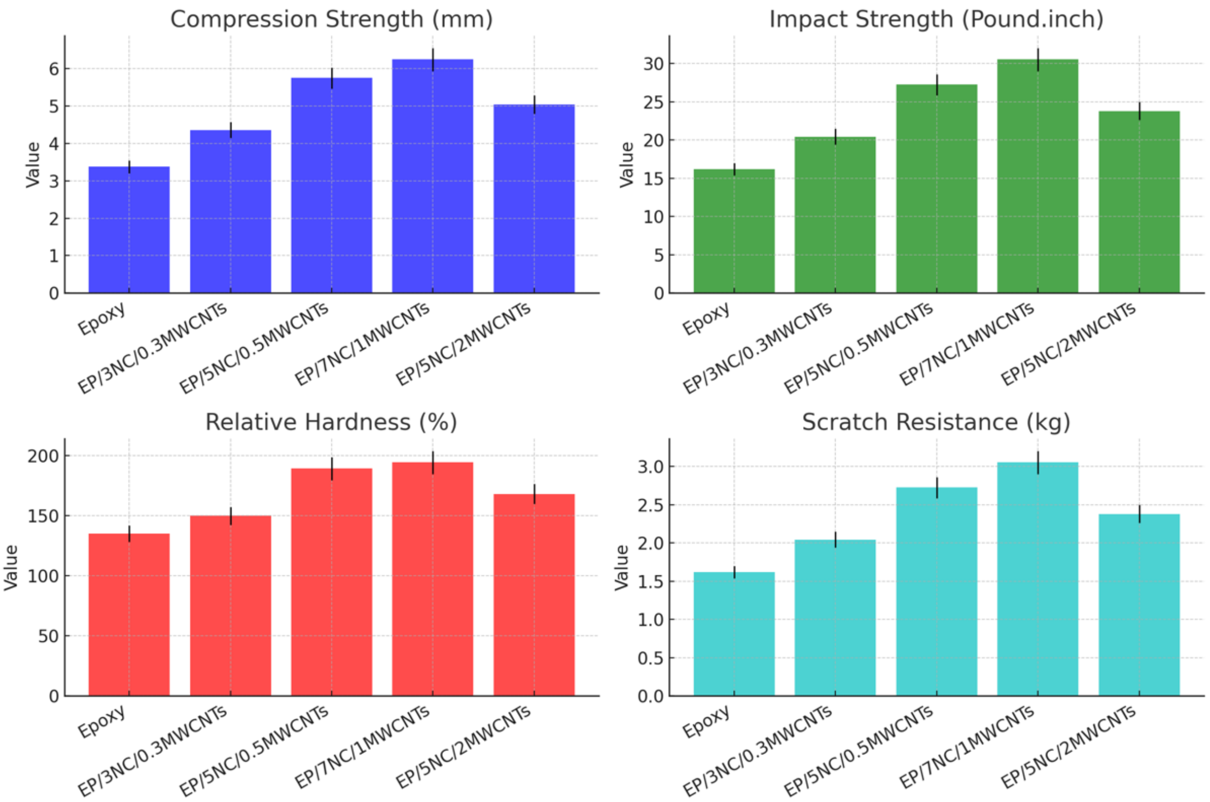

Figure 6 Mechanical properties of nanocomposite coating materials: EP/3NC/0.3MWCNTs: 3.0 wt% Nanoclay/0.3 wt% MWCNTs; EP/5NC/0.5MWCNTs: 5.0 wt% Nanoclay/0.5 wt% MWCNTs; EP/7NC/1.0MWCNTs: 7.0 wt% Nanoclay/1.0 wt% MWCNTs; EP/5NC/2.0MWCNTs: 5.0wt% Nanoclay/2.0 wt% MWCNTs.

Overall, the enhancement in the mechanical properties of epoxy nanocomposite coatings can be attributed to the uniform dispersion and interaction between nanoclay, MWCNTs, and the epoxy matrix, as confirmed by SEM, TGA, and XRD results.

Fire retardant properties of nano composite coating materials

The results from (**Figure 6**) indicate that the limiting oxygen index (LOI) of pure epoxy is the lowest, around 20 %, demonstrating poor flame retardancy.

With the addition of nanoclay (NC) and multi-walled carbon nanotubes (MWCNTs), the LOI value significantly increases, reaching its peak at EP/3NC/0.5MWCNTs, approximately 36 %. This enhancement can be attributed to the uniform dispersion and synergistic effect between nanoclay and MWCNTs, forming a protective barrier that hinders flame propagation. However, when the MWCNT content is increased to 1 and 2 %, the LOI decreases, possibly due to the agglomeration of MWCNTs, which reduces flame retardant efficiency. These findings suggest that the combination of nanoclay and MWCNTs can significantly improve the flame retardancy of epoxy composites, but the composition must be optimized for the best performance, with EP/3NC/0.5MWCNTs being the most effective formulation in this study.

The UL-94V (See **Figure 7**) test results indicate that the flame retardancy of epoxy composite samples significantly improved when incorporating nanoclay and MWCNTs. Neat epoxy was classified as Not Rated, demonstrating its high flammability and inability to self-extinguish within the standard timeframe. When 3.0 - 7.0 % nanoclay (NC) and 0.3 - 2.0 % MWCNTs were added, flame retardancy was enhanced, with most samples achieving V-1 rating. Notably, the EP/5NC/0.5MWCNTs sample achieved a V- 0 rating, indicating that the optimal combination of nanoclay and MWCNTs significantly improved fire resistance.

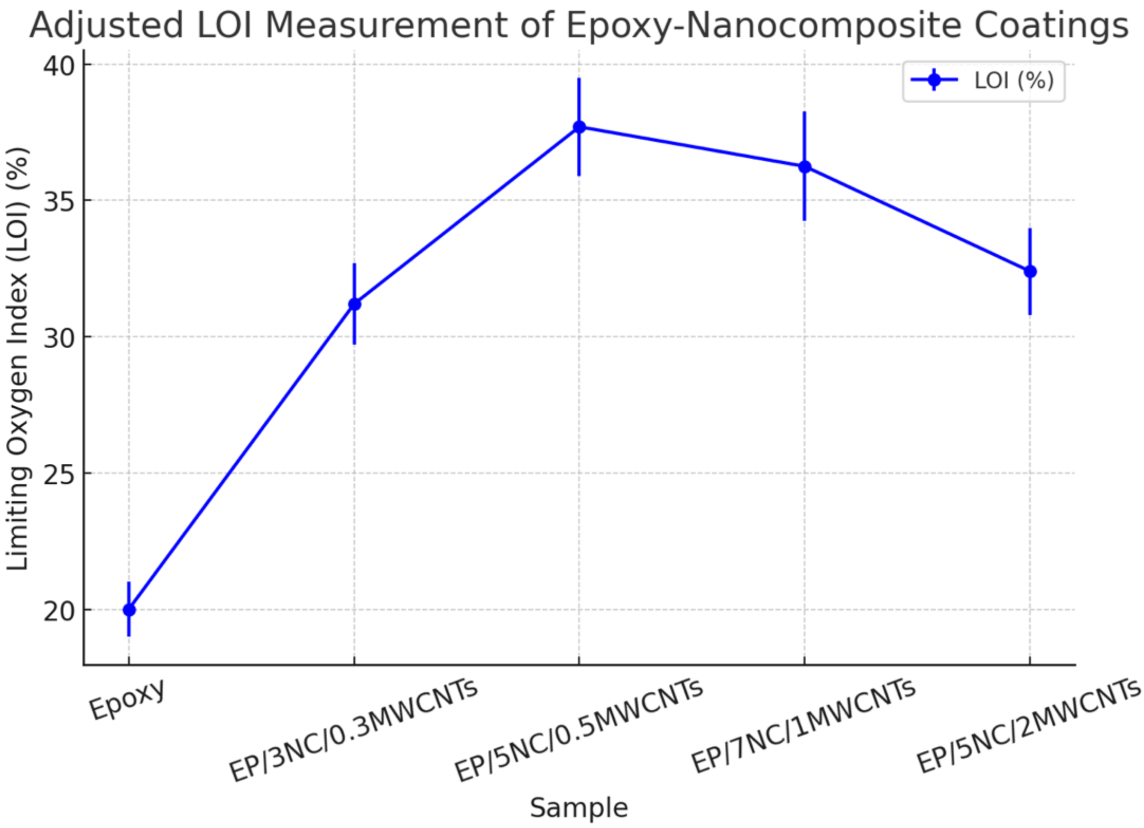

Figure 7 Limiting Oxygen Index (LOI) of Epoxy/Nanoclay/MWCNTs NanoComposite Coatings.

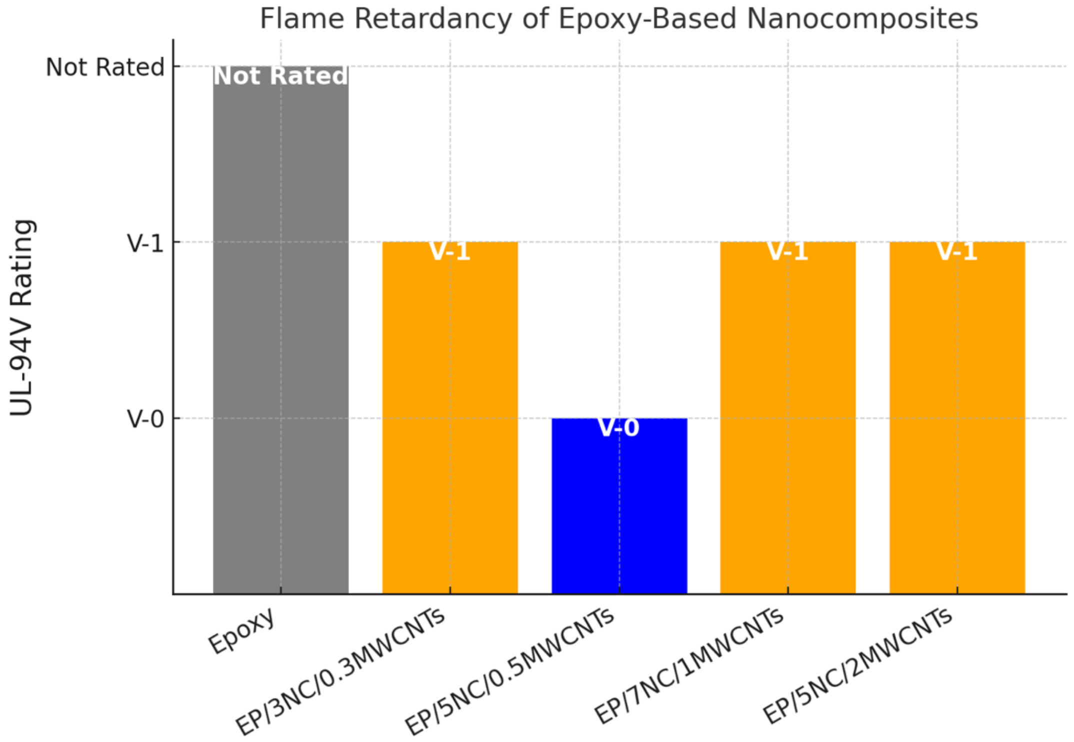

Figure 8 UL 94 V of Epoxy/Nanoclay/MWCNTs NanoComposite Coatings.

This improvement mechanism is elucidated through mechanical, SEM, TGA, and XRD analyses. Mechanical test results revealed that incorporating an appropriate amount of nanoclay and MWCNTs enhanced tensile and flexural strength due to the well-dispersed reinforcing particles, which improved mechanical properties and slowed down fire propagation. SEM images showed that at the optimal concentration (5.0 % NC and 0.5 % MWCNTs), the reinforcing phase was uniformly distributed, forming a robust network that reduced material degradation under high temperatures. TGA analysis demonstrated that the decomposition temperature of nanoclay- and MWCNTs-containing samples was significantly higher than that of neat epoxy, confirming that the nanocomposite system delayed thermal degradation, prolonged thermal stability, and formed a more effective char layer. Notably, the EP/5NC/0.5MWCNTs sample exhibited the highest decomposition temperature, aligning with the UL-94V test results. Additionally, XRD analysis confirmed that nanoclay was well dispersed within the epoxy matrix, forming a homogeneous nanocomposite structure that enhanced both mechanical properties and flame retardancy. Overall, nanoclay contributed to the formation of a protective char layer during combustion, while MWCNTs acted as a thermal barrier, reducing the decomposition rate of epoxy. This synergistic mechanism enabled the material to achieve V-0 classification, highlighting its high potential for applications requiring superior flame retardancy.

From the results in (**Figure 8**), it can be observed that the flame extinguishing time (t_1 and t_2) clearly reflects the flame retardancy of the composite samples. The EP/3NC/0.3MWCNTs sample exhibits the longest burning time (t_1 = 18.0 s, t_2 = 20.0 s), indicating poor flame resistance, especially after the second ignition, where the burning time increases, suggesting that the material does not form an effective protective layer. In contrast, the EP/5NC/0.5MWCNTs sample has the shortest burning time (t_1 = 2.3 s, t_2 = 3.5 s), demonstrating superior flame retardancy due to the effective formation of a protective layer. The EP/7NC/1MWCNTs sample shows a significant reduction in burning time compared to EP/3NC/0.3MWCNTs but remains higher than EP/5NC/0.5MWCNTs (t_1 = 12.0 s, t_2 = 14.0 s), indicating that increasing the content of nanoclay (NC) and multi-walled carbon nanotubes (MWCNTs) can enhance flame retardancy but has not yet reached an optimal level. Meanwhile, the EP/5NC/2MWCNTs sample exhibits a lower burning time than EP/7NC/1MWCNTs (t_1 = 8.0 s, t_2 = 9.0 s) but remains higher than EP/5NC/0.5MWCNTs, suggesting that when the MWCNTs content increases to 2 %, dispersion within the epoxy matrix may be affected, reducing the effectiveness of the protective layer.

Overall, the EP/5NC/0.5MWCNTs sample achieves the best flame-retardant performance, with the shortest burning time in both ignition tests, indicating an effective synergy between nanoclay and MWCNTs in forming a protective layer. The flame-retardant mechanism can be proposed based on the combination of nanoclay, which acts as a physical barrier limiting heat and flammable gas propagation, and MWCNTs, which support the formation of a stable char layer that protects the epoxy matrix from thermal degradation. When combined at an appropriate concentration (5.0 % NC and 0.5 % MWCNTs), these components significantly improve the flame resistance of the composite material.

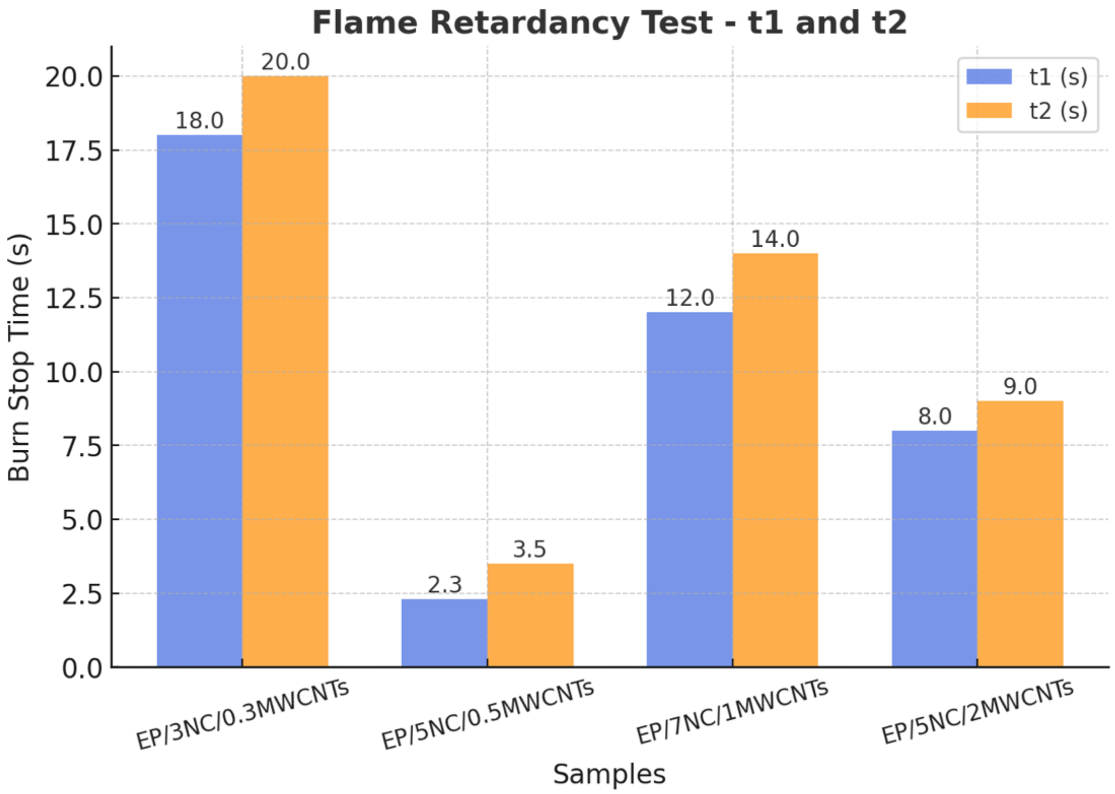

Figure 9 Flame Extinguishing Time for First (t_1) and Second (t_2) Ignition of Composite Samples.

Conclusions

This study successfully fabricated epoxy nanocomposite coatings incorporating nanoclay and multi-walled carbon nanotubes (MWCNTs) at various ratios to enhance mechanical properties, thermal stability, and flame retardancy. The combination of high-speed mechanical stirring (3,000 rpm for 3 h) and probe sonication (90 min, 20 kHz) ensured uniform dispersion of nanoparticles within the epoxy matrix, minimizing agglomeration and maximizing reinforcement efficiency.

The study confirms that the epoxy coating containing 5 % nanoclay I.30E and 0.5 % multi-walled carbon nanotubes exhibits the best mechanical properties and flame retardancy. This optimized sample demonstrates an increased decomposition temperature of 350 °C, compared to 310 °C for pure epoxy, and significantly higher residual char at 500 °C. The reinforcement enhances tensile strength by 35 % and impact resistance by 27 % compared to neat epoxy. XRD analysis indicates the best dispersion of nanoclay in this system, contributing to enhanced thermal stability and mechanical performance.

Future research should focus on investigating different nanofiller ratios, incorporating additional inorganic or organic flame retardants to further optimize the fire resistance of the material. Moreover, long-term durability assessments under harsh environmental conditions are necessary to expand practical applications in industries such as protective coatings and fire-resistant materials.

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Declaration of Generative AI in Scientific Writing

The authors declare that generative AI tools were used only to improve the readability and language of the manuscript. These tools were applied with full human oversight and control. The authors remain fully responsible for all scientific content, analysis, and conclusions presented in the paper. No AI tools were listed as authors or co-authors in this work.

CRediT author statement

Tuan Anh Nguyen: Conceptualization; Methodology; Supervision; Writing – Reviewing and Editing. **Thuy Van Ngo:** Investigation; Data curation; Visualization; Writing – Original draft preparation.

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