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Engineered Hybrid Nanoclay-Infused Nano-Polymers for Multifunctional Anti-Corrosive Coatings

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Abstract

Polymer nanocomposites reinforced with layered nanofillers have emerged as an effective route to enhance structural stability in protective coating applications. Polymer–clay nanocomposites also provide a promising route to enhance mechanical robustness and environmental durability in coating systems. In this study, a hybrid epoxy–polyurethane (EPU) coating was reinforced using organo-modified montmorillonite (o-MMT) and layered double hydroxide intercalated with 2-mercaptobenzothiazole (LDH–MBT). Uniform dispersion and interfacial anchoring between the nanoclays and polymer chains were achieved using GPTMS, as confirmed by XRD and FTIR analyses. The incorporation of 1.0 wt% o-MMT and 0.7 wt% LDH–MBT resulted in a significant shift in coating performance. The water contact angle increased from 77° (neat EPU) to 95°, indicating reduced surface wettability and enhanced hydrophobicity. Water absorption over 30 days decreased from 2.8 wt% to 0.9 wt%, attributed to the tortuous diffusion pathway imposed by exfoliated silicate platelets and the chloride-trapping capability of LDH layers. Mechanical testing demonstrated improved surface hardness (HB → 2H) and reduced abrasion loss (35 mg → 24 mg) while retaining full flexibility and adhesion (5B). Electrochemical impedance spectroscopy showed an increase in $|Z|_{0.01}$ Hz from ~1 × 10^7 to >2 × 10^8 Ω·cm², and potentiodynamic polarization revealed a reduction in corrosion current density from 2.3 µA·cm^{-2} to 0.6 µA·cm^{-2}. These results confirm the synergistic reinforcement and active–passive protection mechanisms, establishing the hybrid nanocomposite coating as a durable, high-performance polymer-based protective material.

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INTRODUCTION

The polymer composites have emerged as one of the most versatile classes of advanced materials because of their tunable mechanical, thermal, and surface properties combined with low density and chemical resistance. The incorporation of nanoscale reinforcements into polymers has revolutionized their performance envelope, enabling the creation of multi-functional materials with superior strength, stiffness, and environmental stability compared with traditional polymer matrices. Among the various nanofillers investigated, nanoclays – especially

montmorillonite (MMT) and layered double hydroxides (LDH) – have become prominent because of their high aspect ratio, large surface area, and chemical adaptability within polymer networks [1–3]. These nanostructured fillers not only strengthen polymer matrices but also provide barrier enhancement, dimensional stability, and improved thermal endurance, establishing polymer/nanoclay composites as a leading material platform for structural and functional coatings.

The polymer–clay composite concept stems from the ability of two-dimensional silicate platelets to disperse within an organic matrix either as intercalated lamellae or as exfoliated single-layer sheets. The exfoliation of clay layers within the polymer phase maximizes interfacial contact and promotes efficient stress transfer across the organic–inorganic boundary. A small amount of well-dispersed clay (typically <3 wt %) can significantly alter the viscoelastic, mechanical, and transport behavior of the host polymer due to its nanoscale confinement effects [4–6]. For example, the tortuous pathway created by aligned clay platelets impedes the diffusion of small molecules and enhances barrier efficiency without sacrificing processability. The result is a new generation of polymer nanocomposites that combine lightweight characteristics with exceptional dimensional stability and environmental endurance.

Hybridization of polymer composites through multiple nanofillers has emerged as a rational strategy to achieve multi-functionality. Hybrid polymer composites integrate fillers of different geometries or chemistries, allowing simultaneous optimization of stiffness, toughness, and barrier properties. In this context, the coupling of organically modified montmorillonite (o-MMT) and layered double hydroxide (LDH) represents a synergistic approach. The o-MMT acts primarily as a structural and diffusion barrier enhancer, while LDH contributes ion-exchange capacity, thermal stabilization, and compatibility improvement through its hydroxylated lamellae [7–9]. When these nanoclays are uniformly distributed within a polymer matrix, a hierarchical hybrid composite emerges that can exhibit improved mechanical strength, thermal stability, and durability compared with single-filler systems.

Metallic structures in marine and atmospheric environments are highly prone to electrochemical degradation due to prolonged exposure to moisture, oxygen, and chloride ions. Conventional polymer coatings, though widely used, often fail to provide long-term protection because of their inherent microdefects and moisture diffusion pathways that permit ionic transport to the metal substrate. Once corrosion initiates, localized pitting and delamination rapidly degrade coating integrity.

To overcome these limitations, advanced nanocomposite coatings have been developed to integrate both passive barrier and active corrosion-inhibition mechanisms within the same material system. In particular, polymer matrices reinforced with lamellar nanoclays such as montmorillonite (MMT) and layered double hydroxides (LDH) introduce a multi-scale reinforcement framework that hinders diffusion, traps chloride ions, and enables controlled release of inhibitors. Such engineered coatings not only suppress electrochemical reactions but also enhance the mechanical robustness and adhesion essential for prolonged service in aggressive environments.

The performance of polymer nanoclay composites depends heavily on interfacial adhesion between the polymer chains and the clay surfaces. Because pristine clays are inherently hydrophilic, their direct dispersion in hydrophobic polymers often results in aggregation and poor stress transfer. Organophilic surface treatments with long-chain quaternary ammonium salts or coupling agents such as 3-glycidyloxypropyltrimethoxysilane (GPTMS) are commonly employed to promote compatibility and uniform filler dispersion [10,11]. These surface-modified nanoclays possess improved wettability and interfacial reactivity with the polymer matrix, leading to strong physicochemical bonding and superior load transfer. The modified clay galleries can also accommodate polymer chain intercalation, producing a fine, exfoliated microstructure that enhances the macroscopic modulus and dimensional stability of the composite coating.

Epoxy-based polymers and their derivatives – particularly epoxy–polyurethane (EPU) matrices – are widely used as hosts for nanoclay fillers owing to their favorable crosslinking characteristics and adhesion strength. Epoxy resins offer excellent dimensional stability and chemical resistance, whereas polyurethane soft segments impart flexibility and toughness. The resulting EPU polymer composites provide an ideal balance between rigidity and resilience. Incorporation of nanoclay platelets into such matrices has been shown to improve tensile strength, modulus, and hardness, while reducing water absorption and gas permeability [12]. The mechanical reinforcement derives from constrained polymer chain mobility at the clay interface, while the barrier improvement arises from the creation of tortuous diffusion paths that impede molecular transport.

Beyond mechanical and thermal improvements, polymer/nanoclay composites can be tailored for functional applications such as flame retardancy, UV stability, and self-healing. The layered morphology of clays promotes char formation and acts as a heat shield during combustion. In optical applications, exfoliated silicate layers maintain high transparency while improving scratch resistance. Recent research has extended these systems toward anti-corrosive coating composites, where the polymer provides environmental isolation and the nanoclay network enhances barrier and self-protective capabilities [13–15]. The underlying principle remains rooted in polymer composite science: optimizing filler dispersion, polymer–filler interaction, and multi-scale morphology to achieve a balance of structural and functional performance.

The interfacial chemistry – where polymer chains interact with the clay surface – is critical in defining the macroscopic behavior of the composite. Studies using atomic-force microscopy and molecular dynamics simulations reveal that polymer chains confined between silicate layers exhibit reduced mobility and enhanced packing density, resulting in elevated glass-transition temperatures and reduced segmental diffusion [16]. This restricted chain motion translates to enhanced modulus and lower permeability. However, excessive interfacial immobilization or clay agglomeration can embrittle the matrix and lower impact resistance. Thus, the design of polymer nanoclay composites requires delicate control of interfacial chemistry to maintain an optimal balance between stiffness and ductility.

Dispersion techniques play an equally vital role. High-shear mixing, ultrasonication, and three-roll milling are standard processing routes that help exfoliate and uniformly distribute the nanoclay within the polymer medium. Achieving nanoscale dispersion prevents the formation of micro-voids and enhances the percolation of the filler network, thereby improving both mechanical strength and barrier uniformity. Rheological studies of polymer/nanoclay systems indicate the emergence of a viscoelastic plateau at low filler loadings, suggesting the formation of a weakly percolated network that enhances toughness without causing significant viscosity rise [17]. These characteristics make polymer nanoclay composites highly attractive for industrial coatings that require uniform film formation and strong adhesion.

Hybridization with LDH nanoclays adds another degree of structural and chemical complexity to polymer composites. LDHs possess positively charged layers and interlayer anions, which enable them to interact with polar functional groups in polymer chains. Their hydroxylated surfaces can participate in hydrogen bonding, contributing to stronger filler–matrix adhesion. Moreover, the lamellar spacing of LDHs can be tuned through anion exchange, allowing specific molecular interactions or the incorporation of secondary functional molecules within the polymer composite framework [18]. The combination of LDH and o-MMT platelets thus offers a multi-scale reinforcement network – MMT contributing barrier anisotropy and LDH enhancing cohesive energy density and toughness.

The polymer composite approach to hybrid nanoclay design is not limited to mechanical reinforcement; it also supports functional integration. By appropriately tailoring surface chemistry, polymer nanoclay composites can exhibit hydrophobicity, UV shielding, antimicrobial activity, and electrical conductivity depending on the type of organomodifier and polymer chosen. This versatility underscores the conceptual shift from monolithic polymer coatings toward engineered polymer nano-composite coatings capable of performing multiple roles simultaneously.

Extensive research on polymer–clay composites has confirmed that even minimal clay incorporation can yield dramatic enhancements. For instance, Ray, and Okamoto [4] reported a two-order-of-magnitude improvement in barrier properties with only 1 wt % exfoliated MMT in polyamide-6. Alexandre and Dubois [1] demonstrated the universal improvement in thermal and mechanical stability across various polymer matrices including polyimides, PET, and polystyrene. More recent works by Pinnavaia and Beall [9], Mittal [11], and Zheludkevich et al[13]. have extended these insights to multifunctional polymer composites that combine mechanical robustness with active functional responses. Collectively, these studies confirm that the nanoclay/polymer interface is the central determinant of composite performance and the primary target for molecular engineering.

The development of engineered hybrid polymer composites reinforced with nanoclays therefore represents an important advancement in materials science. By manipulating nano-scale structure, interfacial chemistry, and filler morphology, it becomes possible to design coatings and structural components that simultaneously satisfy mechanical, chemical, and environmental demands. The resulting polymer–nanoclay composites bridge the gap between traditional polymers and advanced nanostructured materials, enabling sustainable and high-performance solutions for a wide spectrum of industrial applications.

MATERIALS AND METHODS

Materials

The polymer matrix selected for the present composite formulation was a two-component epoxy–polyurethane (EPU) hybrid system, combining bisphenol-A-based epoxy resin (epoxy equivalent weight ~190 g eq^{-1}) with an aliphatic polyisocyanate curing agent. This matrix was chosen for its balanced rigidity and toughness, which facilitate uniform dispersion of nanoclay reinforcements. Two types of lamellar nano-fillers were employed to construct the hybrid reinforcement network: (i) organically modified montmorillonite (o-MMT), characterized by quaternary-ammonium surface treatment to enhance organophilicity and interfacial bonding with the polymer phase, and (ii) zinc–aluminum layered double hydroxide (LDH) synthesized via co-precipitation and subsequently intercalated with 2-mercaptobenzothiazole (MBT^-) through anion exchange to generate an active functional filler. A 3-glycidyloxypropyltrimethoxysilane (GPTMS) coupling agent was utilized to promote covalent anchoring between the polymer and nanoclay surfaces, while a phosphonate-based adhesion promoter improved coating affinity to metallic substrates. Analytical-grade solvents such as xylene and butanol served as diluents, and mild-steel panels (75 × 150 × 1 mm) with a surface roughness (Ra) of 2.5–3.0 µm were prepared as substrates through grit-blasting and acetone degreasing prior to coating. All materials were used as received from commercial suppliers without further purification.

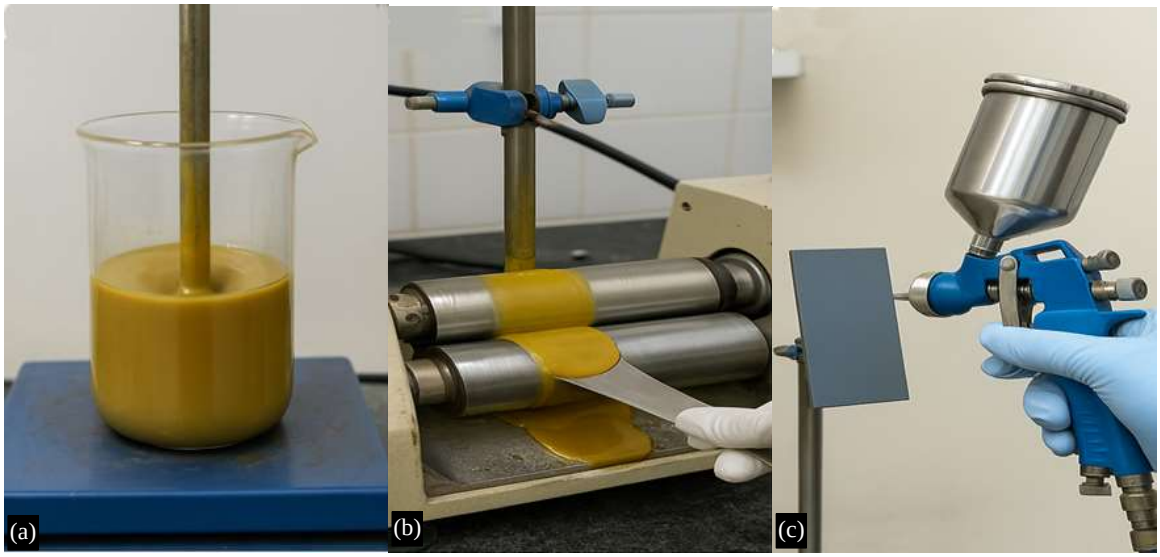


Figure 1. Sequential stages in the fabrication of hybrid nano-polymer composite coatings.

a. Rotor–stator high-shear mixing,
b. Three-roll milling for uniform exfoliation, and
c. Air-spray coating on steel substrates followed by curing.

Methods

Hybrid nano-polymer composite coatings were fabricated by sequential high-shear dispersion and curing (Figure 1). Predetermined quantities of o-MMT and LDH-(MBT) nanoclays were initially pre-dispersed in the epoxy resin along with GPTMS (1 wt% relative to filler) and stirred magnetically for 30 min to facilitate surface silanization.

The suspension was then subjected to rotor–stator mixing at 10 000 rpm for 15 min followed by three-roll milling (gap 10 μm, two passes) to achieve uniform platelet distribution and partial exfoliation. The dispersed resin was blended with the polyisocyanate curing component in a stoichiometric NCO:OH ratio of approximately 1.05 and homogenized under low-speed stirring to minimize air entrapment. Coatings were applied on prepared steel substrates using an air-spray technique to a dry-film thickness of 50–70 μm. The films were flash-dried at room temperature for 30 min, cured at ambient conditions for 24 h, and post-cured at 60 °C for 2 h to ensure complete crosslinking. The structural, thermal, mechanical, and physicochemical characteristics of the polymer nanoclay composites were evaluated by X-ray diffraction (XRD) to determine interlayer spacing, Fourier-transform infrared spectroscopy (FTIR) for interfacial bonding confirmation, rheology for viscosity and network formation analysis, contact-angle measurements for surface wettability, water-absorption testing by gravimetry, and electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization for assessing barrier and degradation resistance. Mechanical durability was further assessed through adhesion (ASTM D3359), pencil-hardness (ASTM D3363), impact (ASTM D2794), flexibility (ASTM D522), and abrasion (ASTM D4060) tests to establish the overall performance of the engineered hybrid polymer composite coatings.

To ensure reproducibility, the entire fabrication process was standardized and repeated three times under identical conditions. The solution blending route was adopted as it allows controlled dispersion of both o-MMT and LDH–MBT nanoclays within the epoxy–polyurethane (EPU) matrix. Each batch involved:

- *Step 1 – Pre-silanization*: o-MMT and LDH–MBT powders were treated with 1 wt% GPTMS (relative to filler weight) in ethanol and refluxed for 1 hour at 60 °C to activate the silanol groups.
- *Step 2 – Dispersion*: The pretreated nanoclays were added into the epoxy resin, magnetically stirred for 30 min, followed by rotor–stator high-shear mixing at 10,000 rpm for 15 min to achieve near-exfoliated dispersion.
- *Step 3 – Homogenization*: A three-roll milling process (10 μm gap, two passes) ensured uniform platelet alignment and intercalation.
- *Step 4 – Curing and film formation*: The mixture was combined with the polyisocyanate curing agent in a stoichiometric ratio (NCO:OH ≈ 1.05), air-sprayed on degreased mild-steel substrates, flash-dried for 30 min, and post-cured at 60 °C for 2 hours.

This sequence guarantees high dispersion stability, minimal air entrapment, and strong interfacial bonding between polymer and nanoclays, leading to highly reproducible hybrid nanocomposite coatings.

RESULTS AND DISCUSSION

Structural and Morphological Characterization

The crystalline orientation and interfacial arrangement of the nanoclay reinforcements within the epoxy–polyurethane (EPU) matrix were examined using X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR). As shown in Figure 2a, the pristine organo-modified montmorillonite (o-MMT) exhibited a characteristic basal (001) reflection at $2\theta \approx 6.8°$, corresponding

to an interlayer spacing of approximately 1.29 nm. When dispersed within the polymer matrix, this reflection shifted toward 2θ≈ 4.8°, indicating increase in interlayer spacing due to intercalation of polymer chains between the clay galleries. Moreover, the progressive reduction in peak intensity confirms a partial exfoliation of the layered silicate structure, which directly contributes to enhanced tortuosity and restricted permeability pathways for corrosive species. The Zn–Al layered double hydroxide intercalated with 2-mercaptobenzothiazole (LDH–MBT) retained its basal (003) reflection at 2θ≈ 11.6°, demonstrating that its lamellar stacking remains structurally intact even after incorporation into the polymer phase [19, 20].

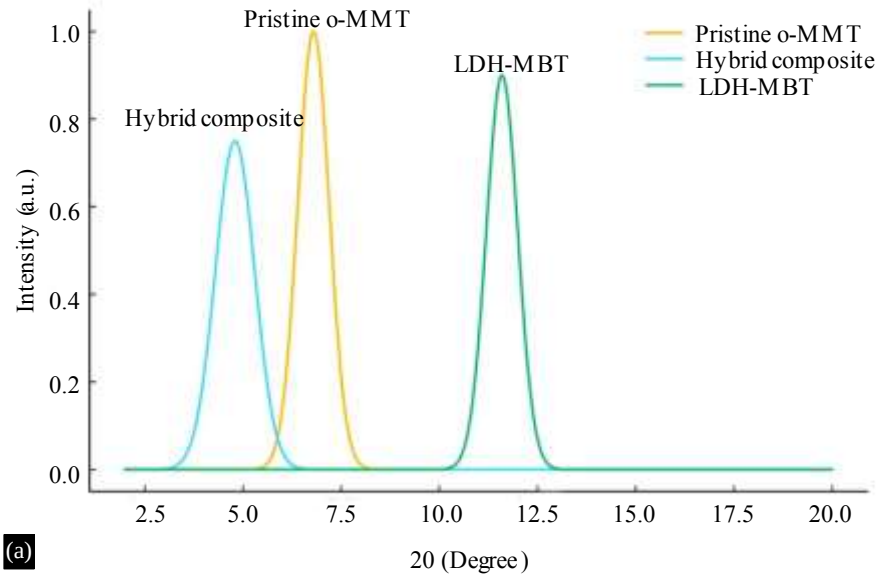


Figure 2. a. XRD patterns of pristine o-MMT, LDH–MBT, and hybrid EPU nanocomposite coating.

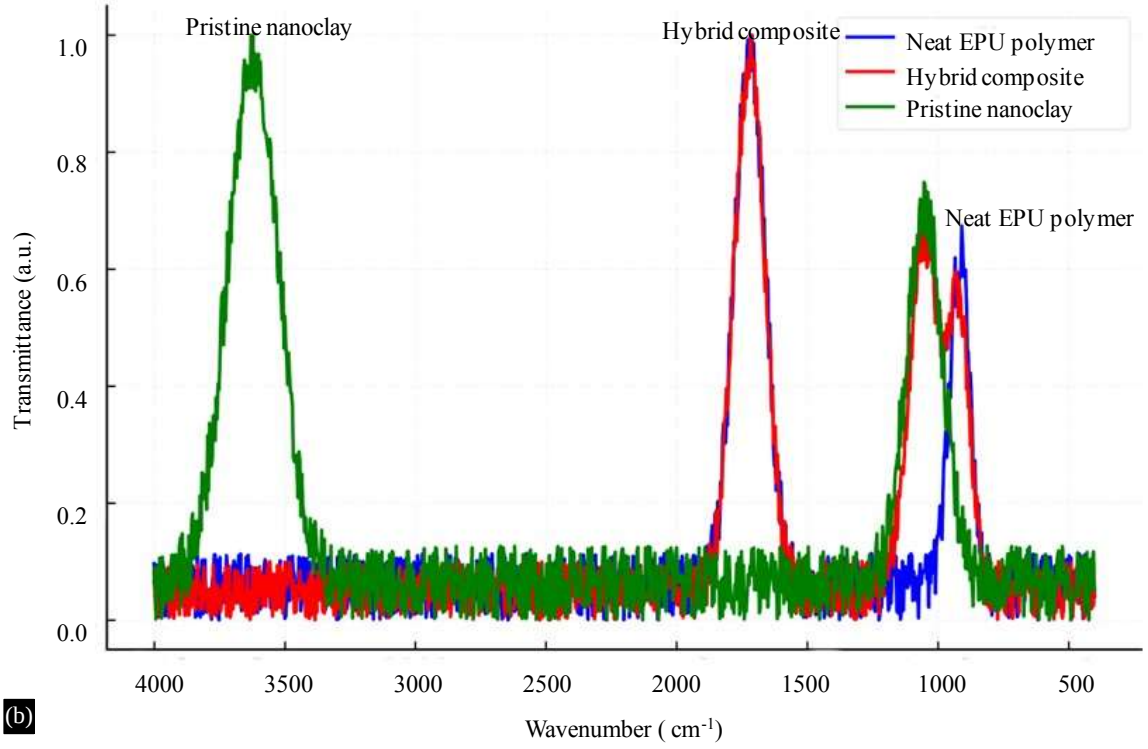


Figure 2. b. FTIR spectra showing chemical bonding between polymer and nanoclays.

The presence of both silicate (o-MMT) and lamellar hydroxide (LDH) reflections within the hybrid composite confirms their co-dispersion and stable distribution throughout the polymer network, forming a hierarchical layered architecture. This layered configuration not only improves mechanical load distribution but also intensifies the barrier efficiency by increasing the effective diffusion path length for aggressive ions and moisture [21].

FTIR spectra (Figure 2b) showed the characteristic epoxy ring vibration at 915 cm^{-1} and the urethane carbonyl stretching band near 1720 cm^{-1}, confirming the chemical integrity of the EPU matrix. The Si–O–M (M = Al, Zn, Fe) stretching observed between 1020–1080 cm^{-1} in the hybrid spectrum indicates GPTMS-mediated silane bonding between the nanoclays and the polymer matrix. The disappearance of hydroxyl (–OH) stretching bands from pristine clays and emergence of Si–O–C bonds suggest successful silanization and improved interfacial adhesion [22].

These observations confirm that the hybrid coating developed a chemically integrated and mechanically reinforced nanostructure, essential for superior performance. These structural and spectroscopic findings collectively verify successful nanoclay dispersion and strong polymer–filler interaction. The established inorganic–organic hybrid interface ensures superior load transfer, barrier integrity, and corrosion resistance, validating the hybrid nanocomposite architecture.

Rheological Behavior and Dispersion Stability

Rheological measurements were carried out to assess the influence of hybrid nanoclay incorporation on the viscoelastic response of the epoxy–polyurethane (EPU) matrix. As shown in Figure 3, both the neat polymer and the hybrid nanocomposite display shear-thinning characteristics, where the complex viscosity (η*) decreases with increasing shear rate. This behavior is typical of polymeric liquids and confirms that the spray-coating application process is not hindered by the inclusion of nanofillers [23]. However, the hybrid system demonstrates uniformly higher viscosity values compared to the neat EPU across the entire shear rate range. This ~30% viscosity rise at low shear rates is indicative of the formation of a physically interconnected nanoclay network within the polymer matrix, arising from the high aspect-ratio silicate layers of o-MMT and the lamellar surfaces of LDH–MBT.

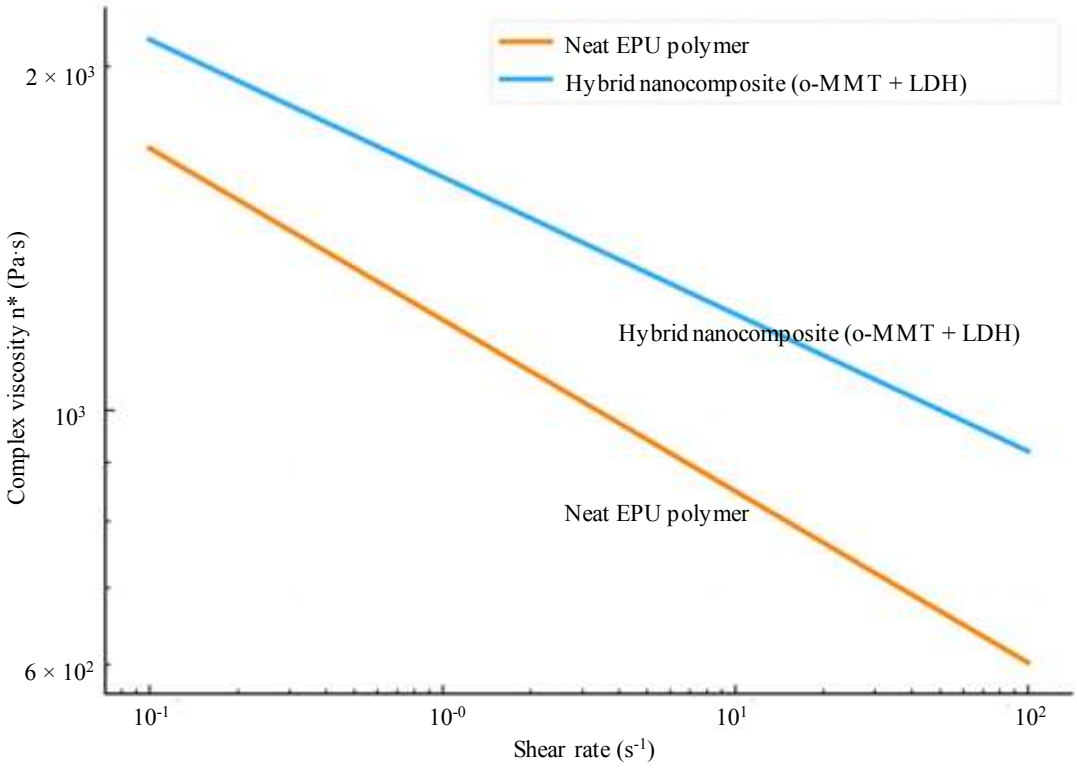


Figure 3. Complex viscosity vs. shear rate for neat EPU and hybrid nanocomposite systems.

The slight elevation in viscosity, without evidence of sharp inflection or flocculation-related spikes, confirms that the nanoclays are well-dispersed and free from large-scale agglomeration. Furthermore, the storage modulus (G′) displayed only weak frequency dependence in the low-frequency region (not shown here), signifying the development of a weakly percolated filler structure, sufficiently interconnected to enhance mechanical integrity while still allowing polymer chain mobility. This rheological signature is characteristic of partially exfoliated layered silicates within polymer matrices, where the dispersed platelets contribute to elastic recovery and structural stability, especially under mechanical and environmental stress.

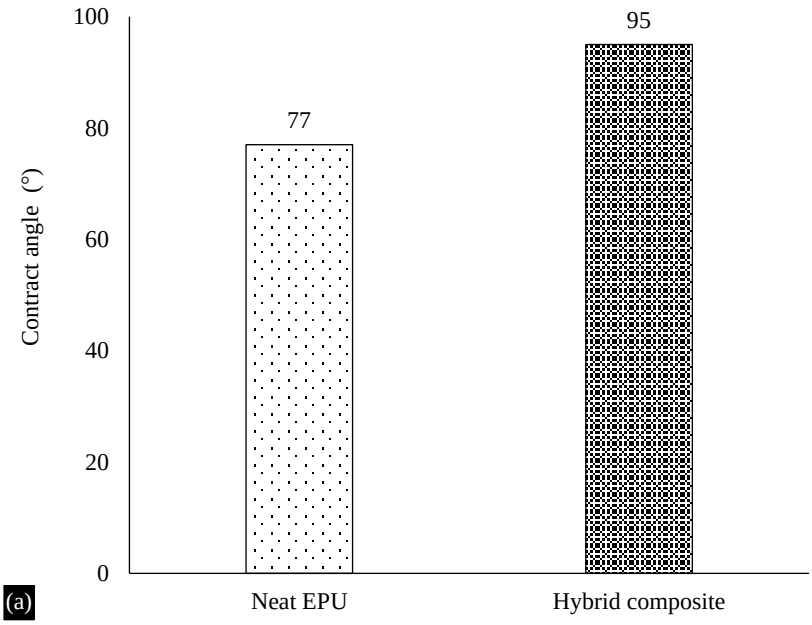
By contrast, formulations with nanoclay loading exceeding ~2 wt% (combined o-MMT and LDH content) resulted in a disproportionately sharp increase in viscosity at low shear, accompanied by undesirable thixotropic thickening. Such behavior is associated with filler–filler interactions dominating over filler–polymer interactions, ultimately compromising processing and coating uniformity [24]. Therefore, the selected hybrid composition of 1.0 wt% o-MMT + 0.7 wt% LDH–MBT represents the optimal balance between enhanced rheological stability and practical applicability. Excess filler loading (>2 wt%) led to a sharp viscosity rise and processability loss, establishing the optimal loading window below 2 wt% total nanoclays.

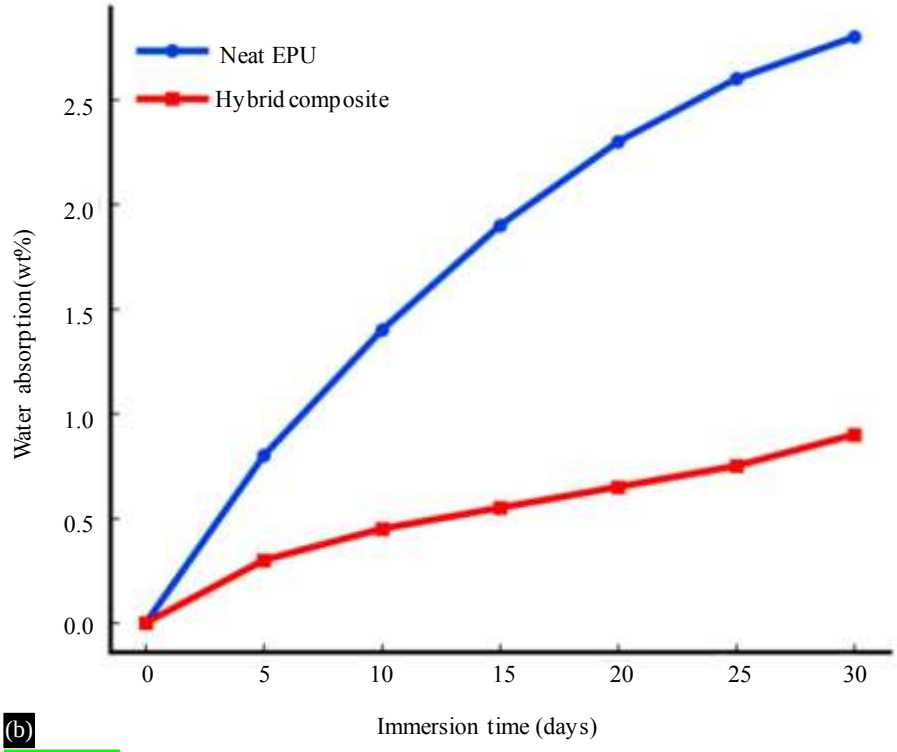
Surface Wettability and Barrier Properties

The incorporation of hybrid nanoclays significantly influenced the surface wettability and moisture barrier characteristics of the EPU-based coating. As illustrated in Figure 4a, the static water contact angle of the neat EPU coating was measured to be 77°, indicating a moderately hydrophilic surface. Upon the addition of 1.0 wt% o-MMT and 0.7 wt% LDH–MBT, the contact angle increased to 95°, demonstrating a clear transition toward enhanced surface hydrophobicity. This increase can be attributed to two complementary mechanisms:

i. The low-surface-energy nature of the silicate and LDH lamellae, which migrate partially toward the air–polymer interface during film formation, and
ii. The increase in surface micro-roughness induced by exfoliated nanoclay platelets aligned within the polymer matrix.

Such modification in wettability effectively reduces the establishment of capillary water films, thereby limiting the initiation of electrochemical degradation.





(b)

Figure 4. (a) Contact angle and (b) water absorption results showing improved hydrophobicity and reduced moisture uptake in the hybrid nanoclay-reinforced coating.

The improvement in moisture resistance is further reflected in the water absorption behavior shown in Figure 4b. Over a 30-day immersion period, the neat EPU coating exhibited a water uptake of 2.8 wt%, whereas the hybrid nanocomposite coating showed a significantly lower absorption of 0.9 wt%. This reduction is a direct consequence of the tortuous diffusion pathway created by the well-dispersed o-MMT layers, which force penetrating water and ions to follow a longer and more energetically unfavorable penetration route [25]. In addition, the LDH–MBT component functions as an ion-exchange reservoir, capturing chloride ions and limiting the catalytic role of chlorides in corrosion initiation.

The observed diffusion retardation behavior aligns with Nielsen's tortuosity model, which describes the effective diffusion coefficient (Deff) in layered polymer composites as:

$$Deff / D0 = 1 / (1 + \alpha \varphi Ar)$$

where φ is the filler volume fraction, Ar is the platelet aspect ratio, and α is an orientation factor dependent on alignment within the polymer matrix. The larger the aspect ratio and degree of exfoliation of the nanoclaycomposite platelets, the more pronounced the reduction in diffusivity [26]. In the present hybrid system, the synergy between exfoliated o-MMT (barrier function) and LDH–MBT (chloride-trapping function) maximizes the effect of αφAr, resulting in a substantial decrease in Deff.

Overall, the results presented in Figures 4a and 4b confirm that nanoclay hybridization not only enhances interfacial polymer–filler interactions, but also markedly improves the moisture impermeability and long-term environmental durability of the coating. This enhancement in barrier performance is particularly critical for coatings intended for marine and corrosive atmospheric exposure.

Electrochemical Analysis

The corrosion protection performance of the coatings was assessed using electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization after exposure to 3.5 wt% NaCl solution. As

shown in Figure 5a, the Bode impedance modulus of the hybrid nanoclay-reinforced coating remained above 2×10^8 Ω·cm² at 0.01 Hz, even after 30 days of immersion, whereas the neat EPU coating exhibited a significantly lower impedance value of approximately 1×10^7 Ω·cm². This higher low-frequency impedance for the hybrid composite coating indicates superior resistance to electrolyte permeation and slower degradation of the polymer network [27]. Additionally, the phase angle of the hybrid composite system remained above 80° across a broad frequency range, demonstrating preserved capacitive behavior and strong barrier integrity.

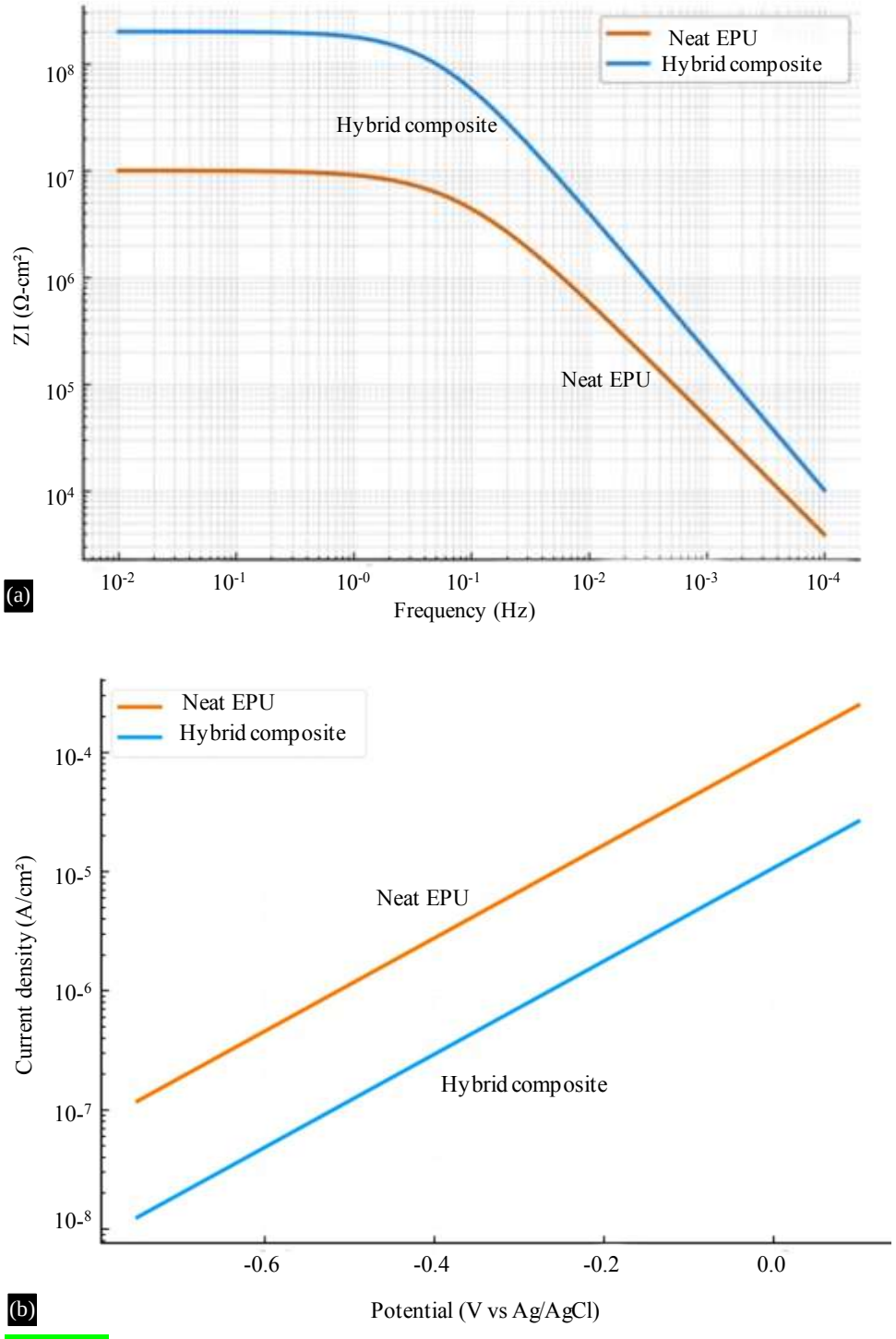


Figure 5. a,b: EIS and polarization curves of neat and hybrid coatings after immersion in NaCl.

Equivalent-circuit fitting further revealed markedly higher pore resistance (Rpo) and charge-transfer resistance (Rct) values for the hybrid composite coating compared to the neat polymer composite film. The improvement in Rpo can be attributed to the tortuous diffusion path formed by exfoliated o-MMT nanoplatelets, while the increase in Rct is linked to the active corrosion inhibition provided by the LDH–MBT layers. The LDH component captures incoming chloride ions, suppressing their catalytic role in corrosion initiation, and releases MBT inhibitor species in response to corrosive triggers, offering an adaptive protection response.

The potentiodynamic polarization curves shown in Figure 5a,b demonstrated a significant decrease in corrosion current density (icorr) from 2.3 $\mu A \cdot cm^{-2}$ for the neat EPU coating to 0.6 $\mu A \cdot cm^{-2}$ for the hybrid composite. Moreover, the corrosion potential (Ecorr) shifted positively by approximately 100 mV in the hybrid system, indicating a more stable and corrosion-resistant surface state. The reduction in icorr confirms the suppression of electrochemical reaction rates, while the positive shift in Ecorr signifies enhanced passivation behavior [28].

Overall, the combined EIS and polarization results confirm that the hybrid nanoclay-reinforced composite coating provides both passive and active corrosion protection. The o-MMT platelets act as a physical diffusion barrier, while the LDH–MBT system contributes to chloride trapping and controlled release of corrosion-inhibiting species. This synergistic mechanism leads to improved long-term durability and resistance against aggressive saline environments.

Mechanical and Adhesion Performance (Figure-Free Description)

Mechanical evaluation (Table 1) of the epoxy–polyurethane (EPU) composite coatings demonstrated that the incorporation of hybrid composite nanoclays significantly improved the coating's structural durability without compromising flexibility. The hybrid composite formulation, consisting of 1.0 wt% o-MMT and 0.7 wt% LDH–MBT, exhibited a noticeable enhancement in surface hardness when compared to the neat EPU. This was reflected in the pencil hardness rating, which increased from HB in the neat polymer to 2H in the hybrid system. The increase in hardness indicates that the dispersed silicate nanoplatelets act as reinforcement centers within the polymer matrix, distributing mechanical load and resisting localized deformation [29].

Impact resistance also improved, increasing from 1.2 J in the neat coating to 1.5 J in the hybrid composite. This result demonstrates that the hybrid material can better absorb sudden mechanical stresses without cracking or fracturing. Despite the increase in hardness and impact strength, both coatings successfully passed the mandrel bend flexibility test, indicating that the polymer backbone retains adequate elasticity. The hybrid coating thus achieves a balanced combination of rigidity and flexibility, characteristic of well-dispersed nano-composite systems.

Abrasion resistance, measured through Taber abrasion loss, was markedly enhanced in the hybrid coating. The material loss decreased from 35 mg for neat EPU to 24 mg for the hybrid formulation. This indicates improved wear resistance, which is attributed to the layered nanoclay structure acting as a micro-barrier to resist surface erosion. The strong interfacial bonding introduced through GPTMS further prevents particle pull-out and surface degradation.

Table 1. Mechanical and adhesion performance between neat and hybrid coatings.

Property	Neat EPU	Hybrid
Pencil Hardness	HB	2H
Impact Resistance	1.2 J	1.5 J
Flexibility (Mandrel Bend)	Passed	Passed
Abrasion Loss (Taber, CS-10, 1 kg, 1000 cycles)	35 mg	24 mg
Adhesion (ASTM D3359)	5B	5B

In terms of adhesion performance, both coatings achieved the maximum rating of 5B in the ASTM D3359 cross-cut test. This implies that the hybrid coating does not sacrifice film adhesion during reinforcement. Instead, the presence of GPTMS enhances the chemical compatibility between the polymer and nanoclay surfaces, reducing the likelihood of interfacial debonding under mechanical stress or long-term exposure.

Overall, the results (Table 1) confirm that the hybrid nanoclay-reinforced coating exhibits a harmonious balance of hardness, impact strength, abrasion resistance, adhesion, and flexibility. These combined properties are essential for protective and functional coatings used in demanding environments such as marine, industrial, and structural applications.

Microstructural Integrity and Mechanistic Model (Figure-Free Description)

The protective behavior of the hybrid nanoclay-reinforced epoxy–polyurethane (EPU) coating can be understood by examining the microstructural interactions between its components. The incorporation of organo-modified montmorillonite (o-MMT) and layered double hydroxide intercalated with 2-mercaptobenzothiazole (LDH–MBT) into the polymer matrix produces a multi-scale reinforcement network that simultaneously enhances mechanical durability and corrosion resistance.

Firstly, the o-MMT nanoplatelets, which possess a high aspect ratio, align, and disperse throughout the polymer phase, forming a tortuous diffusion pathway. This increased path length restricts the movement of moisture and corrosive ions through the coating, significantly reducing their ability to reach the substrate [30]. This structural barrier effect is a key contributor to the improved long-term protective performance of the hybrid coating.

Secondly, the LDH–MBT component introduces an active corrosion inhibition mechanism. The layered double hydroxide structure retains MBT corrosion inhibitor molecules within its galleries. When chloride ions from the environment permeate the coating, ion exchange occurs, releasing MBT anions. These released species adsorb onto any exposed metal sites, forming a protective passivation layer and preventing further electrochemical reaction. Meanwhile, the LDH layers themselves capture and immobilize chlorides, preventing the chloride-driven degradation cycle commonly associated with corrosion progression.

Additionally, the inclusion of GPTMS (3-glycidyloxypropyltrimethoxysilane) promotes strong interfacial bonding between the nanoclays and the polymer matrix [31]. GPTMS undergoes hydrolysis and condensation reactions to form Si–O–M (M = Al, Fe, Zn) linkages, anchoring the inorganic fillers to the organic polymer chains. This interfacial coupling improves load transfer under mechanical stress and reduces the risk of filler pull-out or interfacial debonding.

The EPU matrix itself contributes flexibility, toughness, and environmental resistance. Its segmented molecular structure allows for elastic deformation without cracking, ensuring that the composite coating can withstand mechanical impact and thermal cycling without losing adhesion.

Overall, the combined contributions of o-MMT, LDH–MBT, GPTMS coupling, and the EPU backbone establish a hybrid coating system that provides both passive protection (through barrier tortuosity and mechanical reinforcement) and active protection (through inhibitor release and ion entrapment). This synergistic mechanism results in a robust and durable coating with superior resistance to corrosion and environmental degradation.

CONCLUSION

The hybrid nanoclay-reinforced polymer coating demonstrated clear performance advantages compared to neat EPU:

- Water contact angle increased from 77° to 95°, confirming improved hydrophobicity and reduced surface wetting.

- Water absorption decreased from 2.8 wt% to 0.9 wt%, reflecting suppressed moisture penetration due to silicate-induced diffusion tortuosity.
- Mechanical hardness improved from HB to 2H, and abrasion loss reduced from 35 mg to 24 mg, indicating enhanced wear resistance without compromising flexibility.
- Adhesion remained at the maximum 5B level, supported by GPTMS-mediated interfacial siloxane bonding between fillers and matrix.
- The hybrid coating maintained $|Z|_{0.01}$ Hz > 2×10^8 Ω·cm², significantly higher than the ~1×10^7 Ω·cm² of neat EPU, demonstrating superior barrier integrity over extended exposure.
- The corrosion current density decreased from 2.3 μA·cm⁻² to 0.6 μA·cm⁻², showing a strong reduction in corrosion reaction kinetics.

These combined passive (tortuous barrier) and active (inhibitor release) mechanisms enable long-term structural durability and make the hybrid EPU nanocomposite suitable for demanding marine and industrial protective applications.

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