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Breathable Graphene Oxide-Polymer Composite Membranes With Two-Step Barrier Mechanism Against Nerve Agents

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ABSTRACT

Breathable membranes that reject chemical warfare agents (CWAs) are required for next-generation protective apparel. A dual-function graphene oxide (GO)-polyamine architecture is introduced that addresses the long-standing tradeoff between vapor transmission and CWA selectivity. GO-polymer composite membranes were fabricated on polytetrafluoroethylene (PTFE) supports by pressure-assisted filtration using ethylenediamine (EDA) to reinforce interlayer cohesion and a branched polyethyleneimine (BPEI) overlayer to introduce additional hydrogen-bonding sites and charge-rich domains. Various analytical techniques were used to verify crosslink formation and continuous multilayer architecture. The membranes sustain high water-vapor transmission ($\text{WVTR} > 7000 \text{ g m}^{-2} \text{ day}^{-1}$) while strongly suppressing dimethyl methylphosphonate (DMMP) permeation; in the GO-EDA-PEI configuration no detectable breakthrough is observed. Tests with a live-GD nerve agent yielded $>95\%$ blocking efficiency across all designs and $>99\%$ for GO-EDA-PEI, supporting effective protection across both vapor- and condensed-phase exposure regimes. Under hydration and sonication stresses, EDA crosslinking together with the BPEI capping layer maintains high vapor permeability with strong CWA suppression, without the formation of dense polymer skins that typically compromise breathability. These results demonstrate that GO-polymer composites can couple selective CWA resistance with high vapor transport and operational robustness, meeting practical requirements for protective garments and offering a scalable route to breathable barriers.

1 | Introduction

Despite the Geneva Protocol and the Chemical Weapons Convention, confirmed and alleged chemical agent incidents have continued to be reported in recent conflicts, underscoring the need for practical personal protection [1–3]. Documented examples include the use of sulfur mustard by ISIL in Marea, Syria (2015), as concluded by the OPCW Investigation and Identification Team, and high-profile Novichok nerve-agent poisonings in Salisbury, UK (2018) and in the case of Alexei Navalny (2020).

These events illustrate the capabilities of both state and non-state actors, as well as the enduring operational relevance of chemical threats [4, 5].

Protective ensembles are commonly classified into impermeable, sorbent-based, air-permeable, and selectively permeable architectures [6–9]. Impermeable systems (e.g., butyl-rubber films or film-laminated fabrics) not only deliver broad-spectrum barriers but also block water vapor and air, leading to a heat burden and reduced comfort [6]. Sorbent-based air-permeable systems

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permit air flow through a textile stack and rely on activated-carbon beds for physisorptive capture; however, the sorbent load increases garment weight and bulk and can complicate moisture management [10, 11]. By contrast, selectively permeable membranes (SPMs) are engineered to transmit water vapor while excluding chemical warfare agents (CWAs) through size, shape, solubility, and/or reactive selectivity, thereby enabling a low basis weight and reduced thermal strain for the wearer [8, 12–14].

Despite substantial progress in selectively permeable membranes, a central unresolved challenge remains: achieving effective suppression of organophosphorus transport under both vapor-phase diffusion and liquid or condensed-phase exposure, while preserving high water-vapor permeability under practical operating conditions. In realistic protective scenarios, membranes may encounter both vapor-phase threats and direct liquid contact, necessitating robust performance across multiple transport regimes [6, 7]. Existing GO-based membranes primarily rely on nanoconfined diffusion control and are largely optimized for vapor transport [15, 16]. In contrast, sorbent- or reaction-based systems emphasize capture under liquid exposure but often incur penalties in breathability, weight, or durability [11]. Consequently, most reported systems are inherently tailored to a single dominant transport mechanism, leaving a fundamental gap in the development of phase-adaptive membrane architectures capable of simultaneously regulating dual transport pathways.

Among selectively permeable systems, graphene oxide (GO) offers a combination that is difficult to realize with conventional polymers: atomically thin, 2D lamellae that define angstrom-nanometer galleries for size/solubility selectivity, a chemically addressable surface rich in OH, COOH and epoxy groups for covalent, ionic, and H-bonding modifications, and water-based processability into ultrathin, low-mass laminates by scalable unit operations (vacuum filtration, spray/slot-die) [15–18]. The nanoconfined channels of GO preferentially sorb and transport water while disfavoring bulky, weakly polar organophosphorus species, enabling a high WVTR at low basis weights, consistent with mechanistic studies of transport in layered graphene membranes [19]. Unlike dense polymer barriers that rely on thickness to achieve selectivity, the interlayer spacing (d) and tortuosity of GO can be tuned orthogonally via varying oxidation level, crosslinker length/density, and sheet size to lock the channel dimensions against swelling without forming occlusive skins [20, 21]. In addition, the amphiphilic chemistry of GO supports Janus formats; modest outer-face reduction or fluorosilane grafting imparts oleophobicity, whereas an inner crosslinked hydrophilic core sustains vapor transport and interfacial interactions with nerve CWAs [22–25]. These attributes make GO a particularly lightweight and thermally forgiving platform for selectively permeable protective garments [13, 14, 26].

1.1 | Filtration-Assembled GO Laminates

Compact GO laminates prepared by vacuum/pressure-assisted filtration demonstrated that a high WVTR can coexist with multiday suppression of simulant breakthrough (e.g., dimethyl methylphosphonate (DMMP)), directly demonstrating the intrinsic selectivity of nanoconfined GO channels [27, 28]. Stabilization strategies have realized large-area, high-permeance laminates

and established sub-nano scale control of d -spacing; nevertheless, under hydrated or operational perturbations, swelling-induced instability remains a scale-up challenge, underscoring the need to reinforce interlayer cohesion [29–31].

1.2 | Polymer-Assisted GO Multilayers (Spray/LbL)

Using a spray-assisted layer-by-layer (LbL) route, ultrathin linear polyethyleneimine (LPEI)/GO stacks (≈ 100 nm) can be assembled that lower DMMP vapor transmission while retaining breathability by exploiting the pH-responsive conformation of LPEI, illustrating a simple polymer-GO pathway to selective blocking without heavy sorbents [13]. Related LbL/hydrogen-bonded GO/polymer multilayers tune the intersheet cohesion and defect tolerance through surface-charge control and polymer chemistry, reinforcing the concept while revealing nontrivial uniformity and pinhole challenges for high-throughput, large-area deposition [32–34]. Beyond PEI, bioproduced polymers can drive water-based self-assembly with GO into nacre-like laminates (e.g., GO/PGA/Ca²⁺), achieving substantial mechanical reinforcement via hydrogen-bonding and ionic crosslinks; however, vapor/gas transport and CWA permeability have not been evaluated [35]. Finally, chemical barrier function with maintained vapor transport has recently been demonstrated by GO/polyurethane (PU)-layered SPMs, extending the GO/polymer palette to flexible garment substrates, although quantitative CWA metrics and long-area defect control remain active development items [36, 37]. Across these references, translation to garment-scale SPMs will require standardized agent-level permeation benchmarks, quantitative defect metrology with industry-compatible deposition to ensure uniformity without WVTR penalties, and validated durability under hydration/abrasion/wash and humidity cycling to suppress swelling and intersheet slippage while keeping process complexity and cost in check.

1.3 | GO-MOF Hybrids and MOF-Textile Composites (Complementary Architecture)

In parallel with selectively permeable GO-based laminates, extensive efforts have been made on waterproof-breathable protective membranes based on polymer composites and electrospun nanofibers, including PTFE-coated high-temperature polymer nanofiber membranes and related WB architectures [38, 39]. These studies have demonstrated the capability of polymer-based composite membranes to combine hydrostatic resistance with high vapor permeability through microporous transport mechanisms, providing valuable design principles for breathable protective materials. Building on the nanoconfined transport characteristics of GO, GO-metal-organic framework (MOF) laminates couple a thin GO sieving layer with adsorptive/reactive MOF nanophases to suppress permeation while retaining vapor transport [14, 40]. In parallel, MOF-textile platforms achieve air-permeable protection through the reactive capture, dispersion, or growth of Zr-MOFs on fibers to accelerate organophosphorus hydrolysis while maintaining garment-level breathability [41]. Collectively, these studies validate reactivity-assisted selectivity. Importantly, they operate in a different transport regime than

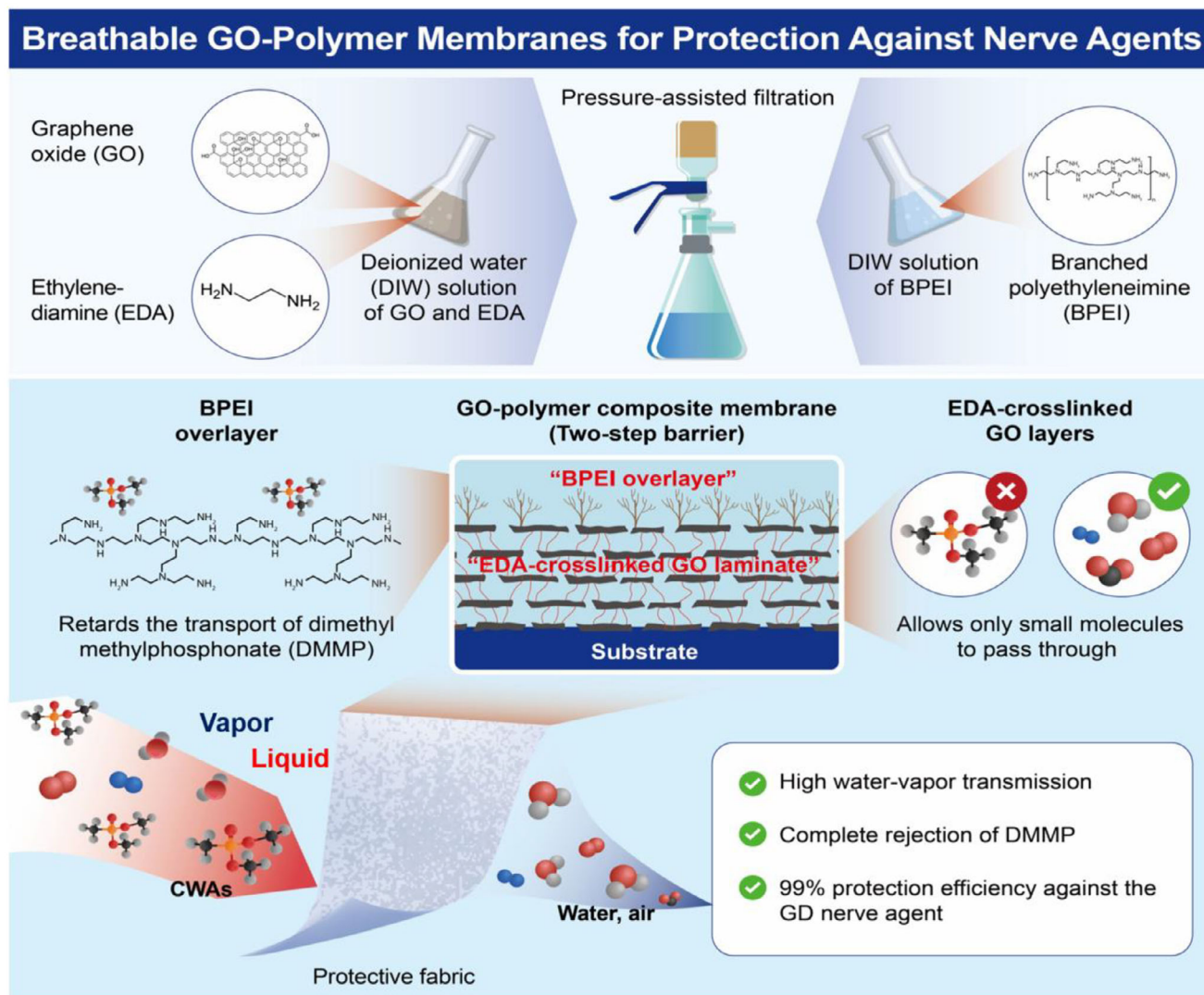


FIGURE 1 | Schematic illustrating fabrication of PTFE/GO-EDA/BPEI membrane for CWA blocking. Two-step GO-polymer membranes combine nanoconfined sieving and interfacial retention, achieving breathable yet nerve-agent-impermeable protection.

selectively permeable barriers and are best viewed as complementary rather than direct competitors. In practice, hybrid layering can couple reactive capture with nanoconfined sieving to balance vapor transport selectivity and mass [14, 40, 42]. Thus, multistep MOF synthesis/anchoring, loading-dependent increases in basis weight, and durability issues during wash/abrasion/humidity cycling remain outstanding challenges [9].

While prior systems integrate diffusion control and capture within a single functional matrix, such coupling can limit independent tuning of transport pathways. To our knowledge, prior GO-based membranes have not explicitly implemented a structurally decoupled architecture separating vapor-phase diffusion regulation from liquid-phase interfacial retention within a single breathable membrane.

To address these limitations, a GO/polymer composite membrane with a two-step barrier was designed (Figure 1). Rather than simply combining diffusion control and sorptive interactions within one matrix, the present design spatially separates nanoconfined diffusion regulation in crosslinked GO galleries

from interfacial molecular retention mediated by an amine-rich overlayer. A thin BPEI overlayer supplies amine-rich hydrogen-bonding/cationic domains that retard organophosphorus transport at the interface, whereas an EDA-crosslinked GO laminate stabilizes interlayer spacing and enforces nanoconfined size and solubility sieving within the gallery network [43, 44].

This functionally decoupled two-step architecture enables independent optimization of dual transport mechanisms and represents a conceptual shift from single-mechanism enhancement toward phase-adaptive membrane design. Importantly, this architecture does not rely on increased thickness, heavy sorbent loading, or dense polymer skins to achieve selectivity, thereby maintaining a low basis weight and high vapor permeability.

Accordingly, we fabricated compact GO-polymer membranes via pressure-assisted filtration using water-based chemicals, minimizing through-thickness pinholes, interlayer delamination, and crack-type defects that could create non-selective leakage pathways.

The optimized GO-EDA-PEI architecture preserves high WVTR while strongly suppressing simulant permeation. In live-GD swatches, no detectable breakthrough was observed within the measurement window. Spectroscopic and structural analyses (FTIR, XPS, SEM, AFM, and XRD) indicate covalent crosslinking and multilayer continuity. Collectively, these results demonstrate a phase-adaptive, lightweight selectively permeable membrane architecture suitable for low-heat-strain protective garments.

2 | Results and Discussion

2.1 | Properties of GO

The density of oxygen functional groups in GO plays a critical role in the formation of multilayers for membrane fabrication and in enabling complexation with various amine-containing molecules. GO synthesized by the Hummers' method exhibited a (001) reflection at a 2θ value of approximately 9.7° in XRD, corresponding to $d_{001} \approx 0.91$ nm, indicating substantial oxidation and interlayer expansion (Figure S1b). XPS analysis further showed that the carbon and oxygen contents were 56.80% and 43.21%, respectively (C/O ≈ 1.31) (Figure S1c). Oxidized carbon contains various oxygen-containing functional groups such as hydroxyl, epoxy, and carboxyl groups. These results indicate that the oxygen functionalities are uniformly distributed over both the surface and edges of the GO sheets. These observations are consistent with the FTIR spectra (Figure S1d). Because of its high density of oxygen functionalities, GO carries a negative charge in aqueous solutions at pH values below 11 [44]. The high level of oxidation and stable anionic nature over a broad pH range suggest that GO can readily form stable complexes with amine-containing molecules such as EDA and PEI. This combination of high functional group density and colloidal stability provides an ideal precursor for the formation of uniform amine-crosslinked lamellae. Image analysis indicates lateral flake sizes on the order of ~ 0.9 μm (median), larger than the pores of the PTFE support, which minimizes pore intrusion and promotes formation of a continuous selective layer (Figure S1a) [13].

2.2 | Properties of PTFE/GO-EDA/BPEI Film

GO-polymer composite membranes were fabricated via vacuum filtration. To prevent solvent-induced wrinkling reported for PES supports (Figure S9), chemically and thermally robust PTFE was selected as the substrate.

The membranes exhibited a bilayer architecture comprising (i) an EDA-crosslinked GO laminate that reinforces interlayer cohesion and suppresses hydration-induced swelling [21] and (ii) a BPEI overlayer rich in primary, secondary, and tertiary amines that can form hydrogen bonds with organophosphorus agents (Figure 1). This “two-step barrier” combines dimensional stability with interfacial selectivity.

Spectroscopic confirmation of crosslinking is shown in Figure 2a. Pristine GO exhibits absorption peaks at ~ 3400 cm^{-1} (O—H stretch), 1728 cm^{-1} (carboxyl C=O), ~ 1620 – 1645 cm^{-1} (aromatic C=C and/or bound-water $\delta(\text{H—OH})$), 1384 cm^{-1} (carboxyl C=O),

~ 1220 cm^{-1} (epoxy C—O), and ~ 1060 cm^{-1} (alkoxy C—O). In PGEB422, PGEB433, and PGEB444 samples, characteristic peaks appear at 1614 , 1525 , and 1371 cm^{-1} , attributed to amide C=O, N—H, and C—N bonds, while the carboxyl C=O peak at 1384 cm^{-1} decreases significantly. This is consistent with amide formation and amine incorporation [45]. Compared to the GO-EDA membrane, the PGEB422 membrane (Figure S2a) exhibits higher intensities of amide/N—H/C—N features, attributable to the amine-rich BPEI overlayer.

XPS analysis further supports these assignments. In the pristine GO membranes, the C1s components are observed as C—C (284.8 eV), C—O from epoxy and hydroxyl groups (286.8 eV), and C—O from carbonyl and carboxyl groups (288.25 eV), with epoxy and hydroxyl groups present in high proportions (Figure 2c). After EDA crosslinking, the C—O peak decreases and a new C—N peak emerges, consistent with the ring opening of epoxy groups and amidation of carboxyl groups (Figure S4) [21]. In the PGEB samples, the C1 spectra shows decreasing C—O and C—C contributions with increasing EDA and BPEI concentrations, and the C—N fraction increases. In addition, a gradual increase in the $-\text{NH}_2$ component in the N 1s spectrum indicates that BPEI undergoes partial amidation with residual carboxyl groups of GO while enriching the surface with free amines that enhance CWA binding selectivity.

To further evaluate the possible structural evolution of GO upon amine incorporation, Raman spectroscopy was conducted (Figure S11). All samples exhibit the characteristic D and G bands of GO, while the I_D/I_G ratio increases slightly from 0.95 (PGEB400) to 1.06 (PGEB444) with increasing EDA/BPEI content. This modest increase reflects enhanced structural disorder associated with amine-induced covalent functionalization, suggesting localized modification of the carbon framework rather than extensive structural reorganization. The attenuation of the 2D and $\text{D}+\text{G}$ bands further suggests partial modification of the sp^2 network. These spectral changes are consistent with epoxy ring-opening reactions and amide bond formation, which locally modify oxygen-containing functional groups and the conjugated carbon network. These Raman observations are supported by complementary XRD and XPS analyses. The increase in interlayer spacing in XRD and the emergence of C—N/amide components in XPS are consistent with amine intercalation and covalent modification of GO (Figure 2g–i).

Morphological characterization by SEM and AFM (Figure 3; Figures S5 and S6) indicates well-aligned lamellae with smooth and continuous surfaces, without evidence of macroscopic pinholes, cracks, or delamination that would result in non-selective leakage. The nanoscale features observed are intrinsic to the lamellar GO-based architecture and correspond to transport nanochannels rather than structural defects.

Interlayer spacing (d_{001}) obtained from XRD (Figure 2b) shifts systematically with increasing amine content: 10.90° , 10.66° , and 10.00° for PGEB422, PGEB433, and PGEB444, corresponding to d_{001} values of 0.811 , 0.829 , and 0.884 nm, respectively. Subtracting the graphitic layer thickness (~ 0.34 nm) gives “free gallery” spacings $\delta = 0.471$, 0.489 , and 0.544 nm, slightly smaller than the kinetic size of DMMP (~ 0.57 – 0.60 nm) [46]. Because d_{001} expands upon hydration, these δ values represent dry-state lower bounds;

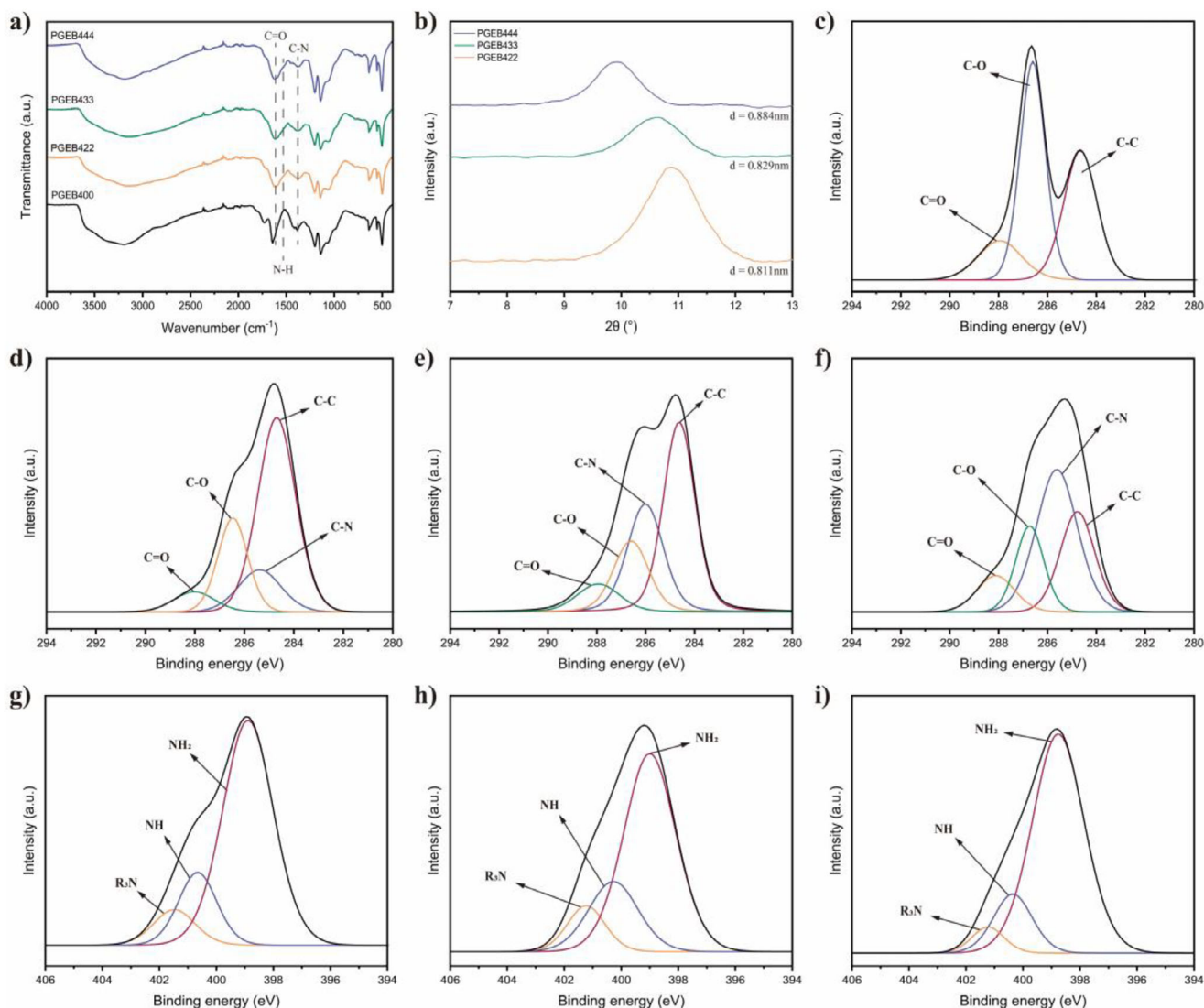


FIGURE 2 | (a) FTIR spectrum of pristine GO and GO-ethylenediamine-branched polyethyleneimine composite membranes. Ethylenediamine reacts with oxygen-containing groups of GO through condensation and nucleophilic addition reactions, forming covalent bonds that interconnect GO nanosheets. BPEI, possessing abundant amine groups, strongly interacts with GO nanosheets to form a secondary adsorption layer, thereby imparting high steric hindrance and enhanced adsorption capacity. (b) XRD spectrum of GO-EDA-BPEI composite membranes in the dry state. The interlayer spacing values, calculated using Bragg's law, are marked at each peak. (c) C1s XPS spectrum of pristine GO membrane (PGE400). (d–f) C1s XPS spectra of GO-EDA-BPEI composite membranes. (g–i) N1s XPS spectra of GO-EDA-BPEI composite membranes (see Table S1 for detail).

thus, rejection arises from the combined effects of channel size, tortuosity, and interfacial interactions rather than steric exclusion alone.

In addition to preserving structural integrity, the number of stacked GO layers can be adjusted by varying the GO areal loading during vacuum filtration. Representative cross-sectional SEM images (Figure S13) suggest an overall increase in laminate thickness with increasing GO loading while maintaining aligned lamellar stacking.

In the present study, however, the GO areal loading was intentionally kept constant when comparing the effects of EDA crosslinking and BPEI modification. Accordingly, the observed variations in transport performance are primarily associated with

interfacial chemical modification rather than systematic changes in overall laminate thickness.

2.3 | Permeability and Selectivity of Membranes

Protection performance across compositions was evaluated by the upright cup method (ASTM E96; 42°C, 25% RH, 24 h) for DMMP vapor transmission and a convective-flow swatch test (TOP-8-2-501) for live-GD (soman) blocking (Figure 4; Figures S7 and S8) [47, 48]. As shown in Figure 4a, the DMMP vapor transmission rate (DVTR) of pristine PTFE is 653 g m⁻² day⁻¹, which decreases to 233 g m⁻² day⁻¹ for PGE400 (GO only; 64% reduction). Incorporation of EDA and BPEI further suppresses DMMP permeation: 77.3 g m⁻²

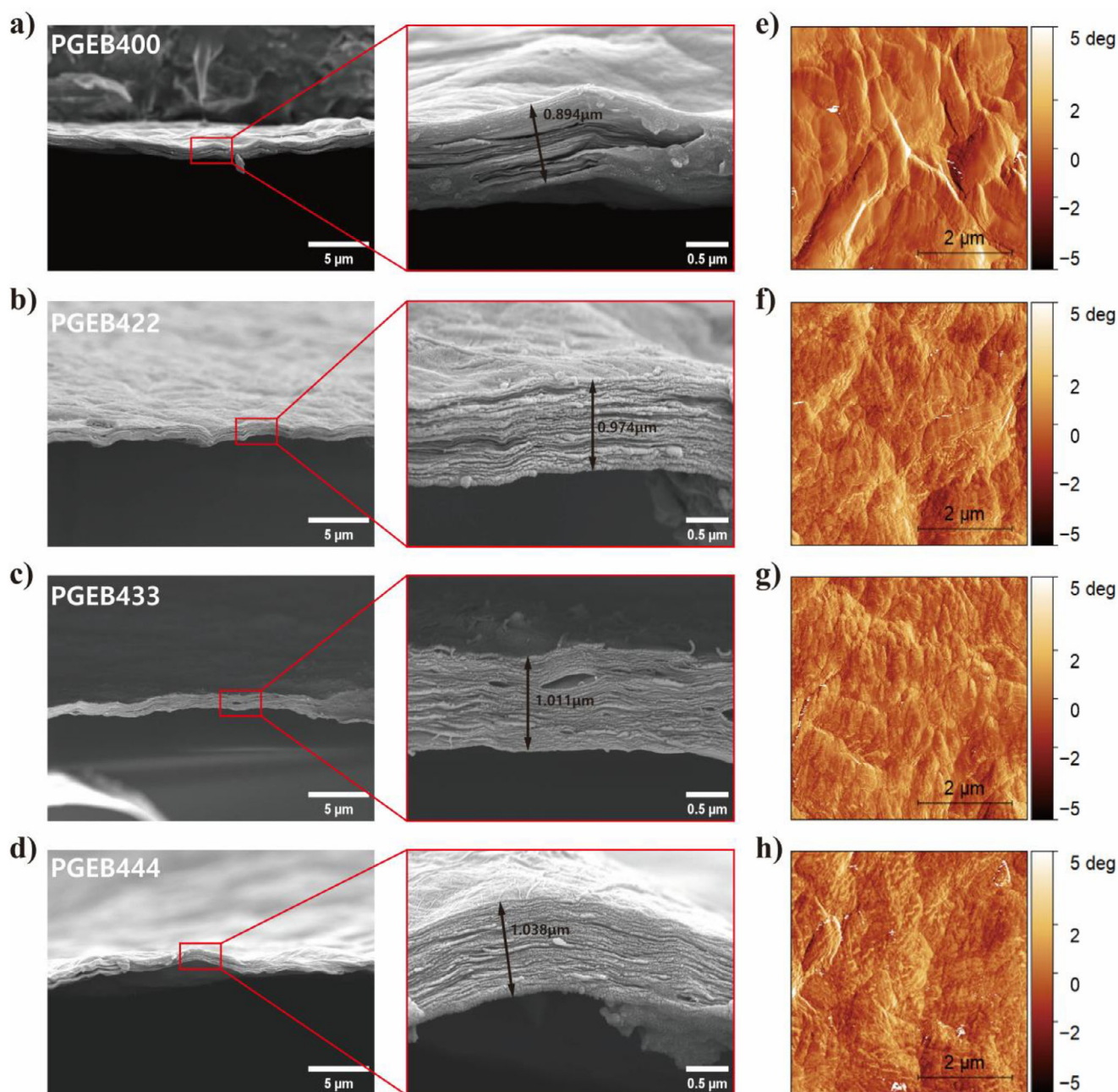


FIGURE 3 | (a–d) Side-view SEM images of PGEb membranes. The film thickness is indirectly observed to increase as the EDA crosslinker content increases. However, owing to the mechanical roughness of the PTFE substrate, the film thickness varies across different measurement locations; therefore, the d-spacing variations were confirmed through XRD analysis. (e–h) AFM images (phase mode) of GO-EDA-BPEI composite membranes on the PES substrate. Due to the high surface roughness of the PTFE substrate, the films were fabricated on a relatively smooth PES substrate for characterization. After incorporation of EDA and BPEI, wrinkled and fibrous morphologies are clearly observed. These differences are attributed to interactions between GO and the additives, in which the crosslinker induces the formation of a structural network between GO layers, resulting in microstructural heterogeneity within the composite.

day⁻¹ for PGEb422 (88% reduction), 28.4 g m⁻² day⁻¹ for PGEb433 (96% reduction), and below the detection limit for PGEb444.

Despite this dramatic DMMP suppression, all samples exhibited high WVTR ≥ 7000 g m⁻² day⁻¹, exceeding the CWA protective clothing standard of 2000 g m⁻² day⁻¹. These results indicate that enhanced DMMP blocking is achieved without compromising vapor permeability.

Selectivity, defined as $\alpha_{\text{H}_2\text{O}/\text{DMMP}} = \text{WVTR}/\text{DVTR}$, increased monotonically with crosslinker/overlayer content (Figure 4b): from ~ 13 (PTFE) to ~ 34 (PGEb400), ~ 100 (PGEb422), and ~ 261 (PGEb433); For PGEb444, the DVTR was below the detection limit, resulting in an effectively very high water/DMMP selectivity within the resolution of the measurement system.

Mechanistically, EDA crosslinking stabilizes GO galleries and mitigates swelling, whereas the BPEI overlayer provides amine-

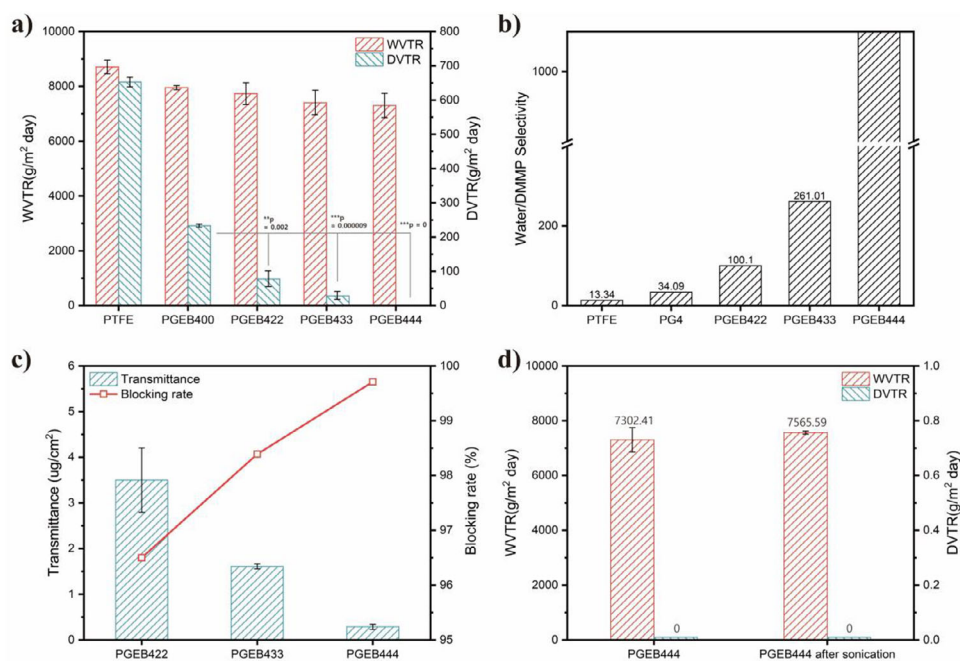


FIGURE 4 | CWA barrier performance, water selectivity, and stability/reusability of PTFE/GO EDA/BPEI membranes in an aqueous environment. (a) Water-vapor transmission rate (WVTR) and DMMP vapor transmission rate (DVTR) for 1 day at 42°C, 25% RH (Red: WVTR, Blue: DVTR). Statistical comparisons are indicated in the graph. (b) Selectivity toward water and DMMP. (c) Swatch test results of PTFE/GO-EDA/BPEI membranes against the live nerve agent GD (Red: blocking rate, Blue: transmittance). (d) Stability of PGE444 membrane after 1 h sonication in water (Red: WVTR, Blue: DVTR). Data are presented as mean $\pm$ SD ($n = 3$). Statistical significance was evaluated using a two-tailed Student's *t*-test. NS, not significant; * $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$.

rich sites for H-bonding and acid-base interactions with the organophosphorus species [49, 50]. These synergistic effects create a two-step barrier (nanoconfined sieving by the GO-EDA framework combined with interfacial retention at the BPEI surface), which accounts for the marked increase in water/DMMP selectivity.

2.4 | GD Protection Property With Swatch

To probe the live-agent-level performance (Figure 4c), dual-flow swatch tests were conducted against soman (military designation GD) following the TOP-8-2-501 protocol (Figure S8) [48]. After 24 h of exposure to GD, the area-normalized cumulative permeation level decreased from 3.50 $\mu\text{g cm}^{-2}$ for PGE422 (lowest EDA/BPEI) to 0.287 $\mu\text{g cm}^{-2}$ for PGE444 (highest loadings), approximately 12 times lower. All three GO-polymer composites achieved $\geq 95\%$ blocking relative to PTFE controls, with PGE444 reaching $\geq 99\%$ within the measurement window under the conditions tested. These agent-level results are consistent with the proposed two-step barrier mechanism (crosslinked nanoconfined sieving and interfacial retention). The combined structural and interfacial effects enable high vapor permeability while maintaining strong protection under convective exposure conditions.

2.5 | Stability Property of Composite Membrane

Membrane durability was assessed by immersing the samples in deionized water, followed by bath sonication for 1 h, after

which the DVTR and WVTR were re-measured. The PGE444 sample was used as the primary specimen; for comparison, PGE400, PGE404, PGE440, PGE422, PGE433, and an otherwise identical laminate on a PES support were subjected to the same protocol to deconvolute the effects of pristine GO, EDA crosslinking, and the BPEI overlay.

As shown in Figure S10, all the samples except PGE444 underwent partial film degradation during sonication. In the PES-supported sample, damage was evident in both the laminate and substrate, underscoring the importance of substrate selection. PTFE provided superior structural integrity. These observations are consistent with the known tendency of GO laminates to swell or delaminate upon hydration, unless the intersheet cohesion is sufficiently reinforced.

Vapor permeation tests were conducted only on the PGE444 sample, which remained intact after sonication. As shown in Figure 4d, the WVTR increases slightly compared to the pretested value, whereas the DVTR remains below the detection limit under the measurement conditions, indicating that the laminate retained its protective function against DMMP under the conditions tested.

To further assess hydrothermal stability under prolonged aqueous exposure, the PGE membranes were immersed in deionized water at 50°C for 24 h (Figure S12). After drying, the permeability was re-measured using the upright cup method. As shown in Figure S12b, the WVTR of PGE444 remained high (7781.59 $\text{g m}^{-2} \text{ day}^{-1}$), while a measurable increase in DVTR was observed (29.15 $\text{g m}^{-2} \text{ day}^{-1}$). Although the DVTR increased

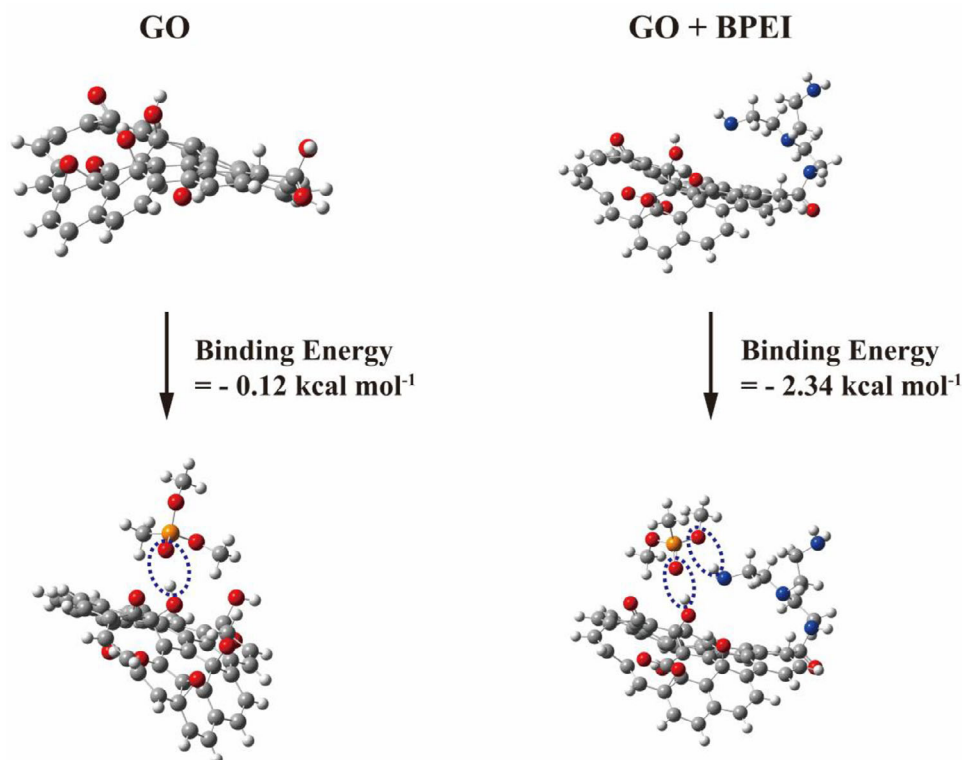


FIGURE 5 | Density functional theory calculation. Optimized geometries and binding energies of DMMP adsorbed on (left) pristine GO and (right) GO-BPEI composite surfaces obtained from DFT calculations. The interaction between DMMP and GO is weak ($-0.12 \text{ kcal mol}^{-1}$), through a single hydrogen bond, whereas incorporation of BPEI introduces multiple hydrogen-bonding sites, strengthening the adsorption ($-2.34 \text{ kcal mol}^{-1}$). The amine-rich polymer enhances dipole–dipole and hydrogen-bonding interactions, effectively immobilizing DMMP on the GO-BPEI surface.

compared to the initial value, the absolute magnitude remains low and the membrane maintained effective suppression of DMMP permeation. The photographic images in Figure S12a further indicate preservation of macroscopic structural continuity after hydrothermal exposure.

EDA crosslinking reinforces the interfacial bonding between the PTFE substrate and the GO nanosheets as well as between adjacent GO layers. In addition, the PEI layer provides supplementary crosslinking, which further stabilizes the GO-EDA film, thereby contributing to enhanced structural stability under aqueous and mechanical perturbation.

2.6 | Density Functional Theory (DFT) Calculations

DMMP, a simulant of the nerve agent GD, contains P–O and P–OR functional groups capable of forming hydrogen bonds, enabling interactions with the hydroxyl groups on GO and the amine groups on BPEI before permeation through the membrane. To evaluate the contribution of BPEI to DMMP adsorption, DFT calculations were performed (Figure 5). The results showed that the binding energy of DMMP on the GO-BPEI surface ($-2.34 \text{ kcal mol}^{-1}$) is substantially larger in magnitude than that on pristine GO ($-0.12 \text{ kcal mol}^{-1}$), indicating stronger interactions with the amine-rich polymeric layer. Moreover, the number of hydrogen bonds increases from one to two, confirming that the molecular adsorption capability is enhanced through hydrogen-bonding

and dipole–dipole interactions. These theoretical findings are consistent with the experimentally observed low DVTR of the GO-EDA/BPEI membrane. Therefore, the superior protective performance of the GO-EDA/BPEI membrane can be attributed to both the size-sieving effect of GO and cooperative hydrogen-bonding interactions predicted by DFT, which effectively immobilize DMMP molecules on the polymer-functionalized GO surface.

2.7 | Performance Benchmarking Against Conventional and GO-Based Protective Membranes

As summarized in Table 1, traditional dense polymer barriers such as polyurethane or butyl rubber films provide effective chemical blocking but inherently suffer from severely reduced water-vapor permeability, leading to substantial thermal burden [49]. Sorbent-based air-permeable systems, including activated-carbon textiles, enable high air and vapor transport but rely on bulk adsorption capacity, resulting in increased weight and limited operational lifetime [10, 11]. GO-based laminates and GO/polymer selectively permeable membranes overcome these limitations by exploiting nanoconfined diffusion pathways to suppress vapor-phase transport while maintaining high breathability; however, their performance has been primarily evaluated under vapor-phase conditions, and long-term stability under liquid or condensed-phase exposure remains an area of active investigation, particularly with respect to swelling or interfacial stability [13, 43–45]. In contrast, the present GO-EDA-BPEI

TABLE 1 | Comparative overview of representative protective membrane systems for CWA mitigation, including dense polymer barriers, sorbent-based systems, and GO-based selectively permeable membranes. Performance metrics such as vapor-phase suppression, resistance to liquid or condensed-agent exposure, and breathability are compared to highlight the intrinsic protection-permeability trade-off.

Membrane system	Vapor-phase agent resistance	Liquid-phase agent resistance	WVTR/breathability	Key limitations	Refs.
Dense polymer barriers (butyl rubber)	High	High	Low	Severe breathability penalty	[49] Kim et al., Chem Rev 2011
Sorbent-based air-permeable systems (activated carbon)	Moderate	High	High	High weight, limited capacity	[11] Sharma et al., 2019
Electrospun WB nanofibrous membrane (polymer composite)	Not evaluated for CWA	Not evaluated for CWA	High	Microporous diffusion structure	[38, 39] Wang et al., 2025, Yu et al., 2019
responsive membrane (SWCNT + TAM polymer)	High	High	Moderate	Complex fabrication, high cost, scalability issue	[12] Li et al., 2020
LBL membrane (GO/LPEI, SGO)	Moderate	NA	High	Moderate suppression, limited durability	[13, 32] Kim et al., 2022 Kim et al., 2022
GO based membrane (GO/PU)	High	NA	Low	Limited selectivity and breathability	[27] Peng et al., 2020
MOF composite membrane (GO/ZIF-8, GO/Uio-66-NH ₂)	High	High	Low	Requires uniform, Low stability	[14, 38] Song et al., 2022 Kim et al., 2023
Mixed-Matrix Membrane (Zr-MOF/PSf)	Not vapor blocking	catalytic hydrolysis (97% conversion DMNP)	Low	No vapor barrier	[51] Lee et al., 2020
Electrospun nanofiber membrane (PAN/AC/CuO)	NA	Moderate (~60% GD blocking)	High	Adsorption capacity limited	[52] Lee et al., 2022
This work (GO-EDA-BPEI)	High	High (≥99% GD blocking)	High (>7000 g m ⁻² day ⁻¹)	Scalable design (ongoing large-area integration studies)	

membrane integrates nanoconfined diffusion control within a crosslinked GO framework with strong interfacial molecular retention mediated by an amine-rich overlayer, thereby effective suppression under both vapor-phase and liquid-exposure testing conditions examined in this study, while preserving the high water-vapor permeability characteristic of GO-based selectively permeable systems.

3 | Conclusion

In this study, PTFE-supported GO-polymer composite membranes were fabricated using pressure-assisted filtration and evaluated for CWA protection. The incorporation of EDA strengthened interlayer bonding between the GO nanosheets and the BPEI overlayer introduced additional hydrogen-bonding sites, which promoted interfacial retention of organophosphorus species, establishing a functionally decoupled two-step barrier architecture.

The composite membranes exhibited high WVTR values that exceed the standard requirement for protective clothing, and excellent WVTR/DVTR selectivity. In particular, the PGEB444 membrane showed DMMP permeation below the detection limit under the tested conditions and achieved $\geq 99\%$ protection efficiency against GD in the swatch test. Furthermore, hydration and sonication tests indicated that the laminate structure remained mechanically and functionally stable, with only limited variation in permeation performance under the examined environmental conditions. DFT calculations supported these findings, showing stronger binding energies and additional hydrogen-bonding interactions between the DMMP molecules and the amine-rich GO-BPEI surface, thereby providing a molecular-level rationale for the experimentally observed selectivity enhancement. Overall, the proposed GO-EDA/BPEI composite membrane demonstrates a balanced combination of breathability and chemical protection within a lightweight laminate configuration, highlighting the potential of structurally decoupled, phase-adaptive membrane architectures for advanced protective applications.

4 | Experimental Section

4.1 | Materials

Graphite flake (-325 mesh, 99.8%) was purchased from Thermo Fisher Scientific., and potassium permanganate (KMnO_4 , 99.3% purity) were obtained from Samchun. Potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$) was purchased from Duksan. Phosphorus pentoxide (P_2O_5), hydrogen peroxide (H_2O_2 ; 35% purity), sulfuric acid (H_2SO_4 , 98% purity) was purchased from Daejung, hydrochloric acid (HCl , 35.0% purity), and ethylenediamine (EDA) were purchased from Junsei, and branched poly(ethyleneimine) (BPEI; average $M_w \sim 800 \text{ g mol}^{-1}$) was supplied by LS. Dimethyl methylphosphonate (DMMP, 98% purity) was purchased from Sigma-Aldrich. Polytetrafluoroethylene (PTFE) membrane filter ($0.2 \mu\text{m}$ pore, diameter 55 mm) was purchased from Hyundai Micro.

4.2 | Synthesis of GO

Graphene Oxide was synthesized using a modified Hummer's method incorporating a pre-oxidation step [13, 53]. First, graphite flakes (9 g) were added to H_2SO_4 (60 mL) and stirred. $\text{K}_2\text{S}_2\text{O}_8$ (7.5 g) and P_2O_5 (7.5 g) were sequentially added, followed by heating and stirring at 80°C for 5 h. Distilled water was slowly added to the mixture, which was then filtered and washed with distilled water. After drying overnight at room temperature, the pre-oxidized powder was added to H_2SO_4 (60 mL) at 0°C . KMnO_4 (15 g) was added slowly, maintaining the solution temperature below 30°C , followed by stirring at 50°C for 4 h. If the viscosity became too high for the stir bar to rotate, distilled water was gradually added while stirring. Subsequently, H_2O_2 (10 mL) was added to further oxidize any remaining unreacted materials. During this process, the color of the mixture changed to yellow. The resulting product was centrifuged twice with 3 M HCl , and subsequently with a 1:1 (v/v) mixture of distilled water and ethanol until the pH of the supernatant reached pH 6. The sediment was stored in an aqueous state.

4.3 | Fabrication of PTFE/GO-EDA/BPEI Membrane

To prepare the GO-EDA feed, an aqueous GO dispersion was diluted with deionized (DI) water to 0.1 mg mL^{-1} and bath-sonicated for 1 h. EDA was then added to the GO solution at weight ratios (GO:EDA) of 1:0.5, 1:0.75, and 1:1 (based on GO solid), followed by 1 h of sonication to promote dispersion and chemical reaction. Subsequently, a BPEI solution was prepared by dispersing in DI water at a concentration of 0.1 mg mL^{-1} and adjusted to pH 10 using NaOH solution.

A known amount of the GO-EDA mixture was filtered through the PTFE substrate using a glass filtration setup with a vacuum pump ($\Delta P \approx 0.7 \text{ bar}$, gauge). After complete deposition of the GO-EDA layer, the BPEI solution (at the same weight ratio as EDA) was filtered to form a polymeric top layer. The composite-loaded substrate was subsequently rinsed with DI water to remove unreacted polymer residues and then dried in a vacuum oven at 60°C for 2 h to facilitate covalent coupling and laminate consolidation. The membranes were denoted as PGEB(x,y,z), where P is the PTFE support, G is the mass of GO (mg), E is the mass of EDA (mg), and B is the mass of BPEI (mg) used during fabrication; x, y, and z indicate the respective masses.

4.4 | Characterization

The surface roughness of the PTFE/GO-EDA/BPEI membranes was measured by AFM (MFP-3D, Oxford Instruments, USA). The surface morphology of the membranes was analyzed using field-emission SEM (FE-SEM, SIGMA 360, Carl Zeiss, Germany). The presence and structure of the functional groups in the GO-polymer composite films were verified by FTIR spectroscopy in the attenuated total reflectance mode in the wavenumber range of $4000\text{--}400 \text{ cm}^{-1}$ (Invenio-R, Bruker, USA) and XPS (K-alpha+, Thermo Fisher Scientific, Easton, USA). The interlayer distances

of the GO-EDA/BPEI multilayer films were examined using XRD (Mini Flex 600, Rigaku, Japan). Raman spectra were acquired using Raman spectroscopy (XploRA PLUS, HORIBA, France) equipped with a 10× objective (NA = 0.25), a 532 nm laser, and an 1800 g mm⁻¹ grating spectrometer. The laser power was set to approximately 75 mW, and the excitation spot diameter was 2.6 μm. The characteristic peak of crystalline silicon at 520 cm⁻¹ was used as the calibration standard. Each specimen was irradiated for 10 s, and measurements were repeated five times to obtain high-resolution spectra.

4.5 | Water and DMMP Permeability Tests

A vapor transmission test was conducted using the upright cup method based on ASTM E96/E96M (water method; DMMP adapted) [47]. Test cups were charged with 40 mL of the target liquid (water or DMMP), and the membrane was sealed on top using an O-ring and clamp. The experiment was carried out at 42°C and 25% relative humidity for 24 h. Mass was recorded at t_0 and t_{24h} on an analytical balance (± 0.1 mg), and WVTR/DVTR was calculated as

$$VTR = \frac{\Delta m}{At} \text{ (g m}^{-2}\text{day}^{-1}\text{)}$$

where A is the effective test area, and t is the test duration. Selectivity was defined as $\alpha_{H_2O/DMMP} = WVTR/DVTR$. Each condition was tested in triplicate ($n = 3$) and reported as mean $\pm$ SD

4.6 | GD Swatch Test

The protective performance against live-agent GD was evaluated according to TOP 8-2-501A using the dual-flow liquid challenge/vapor penetration (L/V) swatch testing method [48]. All test samples used nylon-cotton fabric as the outer layer, whereas the PGEB membrane under investigation served as the inner layer. The membranes were cut into circular swatches with a diameter of 36 mm and mounted on a test cell. A total of 10 μL of GD was applied in ten aliquots of 1 μL each. According to the testing protocol, different airflow rates were applied to the upper and lower surfaces of the swatch to induce GD evaporation, and the permeation resistance was measured to assess the protective performance.

4.7 | Stability Evaluation

The PGEB membranes with various compositions fabricated in this study together with an identical laminate prepared on a PES support were evaluated for stability. The baseline WVTR and DVTR values were first measured using the upright cup method described above. For short-term aqueous and mechanical stability testing, samples were immersed in DI water and bath-sonicated for 1 h (40 kHz, ambient $23 \pm 2^\circ\text{C}$). After treatment, membranes were rinsed with DI water, lightly blotted, and vacuum-dried at 60°C for 2 h before re-testing. WVTR and DVTR were then re-measured under identical conditions. To further assess hydrothermal stability under prolonged aqueous exposure,

the membranes were immersed in DI water at 50°C for 24 h. After immersion, samples were vacuum-dried at 60°C for 2 h and their WVTR /DVTR measurements were repeated under the same testing conditions.

4.8 | DFT Calculation Methods

All DFT calculations were performed using the Gaussian 16 software package. The GO structure was adopted from a previously published study [54], which provides a well-validated model for oxidized graphene sheets with hydroxyl, epoxy, and carboxyl functional groups. Two model systems were constructed: pristine GO and GO functionalized with BPEI. For the GO-BPEI system, BPEI molecules were positioned on the GO surface to mimic the experimentally crosslinked structure. Geometry optimizations were performed using the B3LYP hybrid functional with the 6-31+G(d) basis set, which includes diffuse functions essential for accurately describing hydrogen-bonding interactions. During optimization, the GO sheet and BPEI backbone atoms were fixed to maintain the experimental laminate structure, whereas the DMMP molecule was allowed to fully relax to determine its optimal binding configuration. Tight convergence criteria were applied with a maximum of 200 optimization cycles to ensure accurate geometries. Self-consistent field (SCF) calculations employ a quadratically convergent SCF procedure with a maximum of 300 cycles to achieve convergence in these large molecular systems. Vibrational frequency calculations were performed for the optimized geometries to confirm that true minima were obtained (no imaginary frequencies) and to compute the zero-point energy corrections.

The binding energy (ΔE) was calculated as

$$\Delta E = E(\text{surface} - \text{DMMP}) - E(\text{surface}) - E(\text{DMMP})$$

where $E(\text{surface-DMMP})$ is the total energy of the optimized complex, $E(\text{surface})$ is the energy of the isolated GO or GO-BPEI surface, and $E(\text{DMMP})$ is the energy of the isolated DMMP molecule, all computed at the same level of theory. Hydrogen bonds were identified based on geometric criteria: H...O distances less than 2.5 Å. All the calculations were performed using 64 processors with 40 GB of memory allocation from a supercomputer system at KISTI to efficiently handle a large system size. The Nosymm keyword was used to prevent reorientation of the molecular system during optimization, maintaining consistency in the analysis of binding modes.

4.9 | Statistical Analysis

The experimental data were presented as the mean $\pm$ SD with a sample size of $n = 3$ per group. The datasets shown in Figure 4a,d were analyzed using a two-tailed Student's t -test in OriginPro (version 2018, OriginLab, USA). Statistical significance was determined at a significance level of $\alpha = 0.05$. P values less than 0.05 were considered statistically significant. Statistical differences were denoted as follows: NS, not significant; * $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section.

Supporting File: adfm74803-sup-0001-SuppMat.docx.