Supplemental Information

Atomically Thin Polymer Layer Enhances
Toughness of Graphene Oxide Monolayers

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S1. Dewetting mechanism of PVA chains on the surface of GO

The HRTEM and AFM data presented in the manuscript show that microscale polymer features beyond the nanostructured PVA network are present on the surface of GO-PVA nanolaminates (Figure 1b). An understanding of the formation mechanisms behind this network can provide insight towards the rational design of nanolaminate systems with novel mechanical properties. Such structures presumably arise through a combination of PVA adsorption at the nanoscale and polymer density fluctuations at the microscale. At the nanoscale, the first monolayer of PVA chains preferentially adsorbs to the oxidized domains through hydrogen-bonding interactions, thus nucleating preferential sites onto which subsequent PVA chains can adsorb. In addition, because the size of the graphitic domains that punctuate the network of oxidized domains is less than the length of an extended PVA chain, some of the PVA chains can presumably bridge across the graphitic domains to connect to other PVA chains on neighboring oxidized domains. This results in the formation of a nanostructured PVA network. The resulting nanoscale heterogeneity (PVA-sparse graphitic and PVA-dense oxidized regions) presumably leads to differential adsorption of PVA at the microscale, and formation of the PVA features observed in AFM images.

In contrast, when PVA is deposited onto reduced GO (rGO) monolayers, under the same conditions used to fabricate GO-PVA nanolaminates (see Methods section in the manuscript), a largely continuous PVA coating is obtained (Figure S1c). The lack of PVA patterns implies that polymer density fluctuations do not occur due to the more homogeneous surface of rGO, which primarily contains graphitic domains and relatively few oxidized domains. Furthermore, the highly graphitic nature of rGO implies that it engages in predominantly van der Waals interactions with PVA, rather than the hydrogen-bonding present in GO-PVA nanolaminates. Interestingly, the PVA coating on reduced GO is punctuated by small pinholes (Figure S1d), suggesting that a small number of oxidized domains serve as surface point heterogeneities that lead to minor polymer density fluctuations and subsequent pinhole formation.
Figure S1. AFM images of GO and rGO modified with PVA of two different molecular weights. (a) Uneven polymer coverage on the surface of a GO monolayer modified with PVA (25 kDa). (b) PVA (25 kDa) aggregating into polymer clusters on the GO surface, suggesting that at higher polymer molecular weight PVA-PVA interactions are favored over GO-PVA interactions. (c) rGO modified with a nearly continuous layer of PVA (6 kDa). (d) Pinholes in the PVA (6 kDa) coating on the rGO surface.

As alluded to in the manuscript, the formation of the hierarchical PVA network may also depend on polymer size. The PVA chains used in this work (~34 nm extended length, molecular weight of 6 kDa) are comparable in size to 3-4 GO oxidized domains, and can engage in extensive hydrogen-bonding with these domains, leading to the even coating of microscale PVA features on the GO surface (Figure 1b). However, the use of longer PVA chains (~140 nm extended length, molecular weight of 25 kDa) results in uneven coverage of PVA on the GO surface (Figure S1a), implying weaker GO-PVA interactions. This is supported by high-magnification AFM images which reveal PVA nanoparticles on the GO surface (Figure S1b), rather than the microscale features observed when shorter PVA chains are used, suggesting that PVA prefers to engage in intramolecular hydrogen-bonding instead of interacting with the GO domains. Together, these data demonstrate that selecting a polymer of appropriate size, that is capable of suitable interactions with GO, can allow unique mechanical properties to manifest in the resulting nanolaminate assembly, such as the microscale crack-bridging reported herein.

S2. EELS characterization of GO monolayers and GO-PVA nanolaminates

A series of control samples (graphene, GO, GO-PVA, PVA, and amorphous carbon) were prepared and characterized via EELS in TEM mode to serve as references for interpreting the EELS data of GO-PVA nanolaminates, as discussed in the manuscript. Single-layer graphene samples, pre-deposited on Au-coated QUANTIFOIL R 2/4 TEM grids, were obtained from Graphenea Inc. (Cambridge, MA). GO and GO-PVA nanolaminate specimens were deposited onto lacey carbon-coated Cu TEM grids (Product #01895, Ted Pella, Redding, CA) via the LB
method. PVA samples were prepared by spin-coating ~8 µL of an aqueous PVA dispersion (30 mg/mL) onto lacey carbon-coated Cu TEM grids at 4000 rpm, with an acceleration of 400 rpm used to reach this final speed.

The bare lacey carbon film of the prepared TEM grids served as the amorphous carbon samples. During TEM experiments, a short exposure time of 0.1 second was used to prevent possible amorphous carbon buildup, which could alter the sample’s plasmon peak position. The plasmon peak positions of the other reference samples were consistently below that of amorphous carbon (25 eV), suggesting there was no significant carbon buildup during experiments, and the obtained peak positions are representative of the non-contaminated control samples.

Previous studies have shown that the position of the $\pi + \sigma$ plasmon peak in the EELS low-loss region (<100 eV) can be used to differentiate carbon-based materials such as graphene, GO, amorphous carbon, and organic polymers. The $\pi + \sigma$ peak in the EELS spectrum of unmodified GO is in good agreement with a previous report, and is significantly right-shifted in comparison to the $\pi + \sigma$ peak of graphene, attributable to the presence of oxygen and the increased number of $sp^3$ carbon bonds in GO. For pure PVA, which has a 2:1 C:O content and only $sp^3$ carbon atoms, the $\pi + \sigma$ peak is at 23 eV (Figure S2). As such, the addition of a PVA layer ($66\% sp^3$ carbon) on top of GO ($\sim 30\% sp^3$ carbon), as present in GO-PVA nanolaminate, should cause the $\pi + \sigma$ plasmon peak of GO to shift to values in the 19-23 eV range. This is indeed observed in the EELS spectrum of GO-PVA nanolaminates, which exhibits a broad feature at ~21 eV (Figure S2). As this feature spans a large 17-23 eV range, it likely comprises individual contributions from GO and PVA.

Based on the aforementioned reference data, the position of the plasmon peak in the EELS spectra of GO-PVA nanolaminates obtained in line-scan mode (Figure 2) can be used to distinguish between the three different domains present: 1) mainly graphitic (graphene-like; $\pi + \sigma$ peak = 15.5 ± 0.5 eV); 2) more oxidized (GO-like; $\pi + \sigma$ peak = 18.0 ± 1.0 eV); and 3) PVA-covered ($\pi + \sigma$ peak = 21.0 ± 0.5 eV). As discussed in the manuscript, the EELS line scan of a GO-PVA nanolaminate was interpreted as showing the preferential adsorption of PVA to the oxidized domains of GO.

![EELS spectra](image)

**Figure S2.** EELS spectra (collected in TEM mode) showing the $\pi + \sigma$ plasmon peaks of graphene, GO, GO-PVA, PVA, and amorphous carbon.
S3. X-ray photoelectron spectroscopy characterization of GO monolayers and GO-PVA nanolaminates

X-ray photoelectron spectroscopy (XPS) experiments were carried out in the Keck II/NUANCE facility at Northwestern University using a Thermo Scientific ESCALAB 250Xi (Al Kα radiation, \( h\nu = 1486.6 \text{ eV} \)) (Thermo Fisher Scientific Inc., West Palm Beach, FL) equipped with an electron flood gun. Samples for XPS analysis were prepared via LB deposition of GO and GO-PVA onto Si wafers (Item #785, 100 mm diameter, p-type, B-doped, single side polished) purchased from University Wafer, Inc. (Boston, MA). XPS data was obtained from three different locations on the surface of each sample, and was analyzed using Thermo Scientific Avantage Data System software (version 5.923), with a Smart background subtracted prior to peak deconvolution and integration.

While EELS can capture the nanoscale chemical composition of GO-PVA nanolaminates, XPS can confirm the adsorption of PVA molecules on GO monolayers over the micron length scale, due to the larger XPS spot size (500 µm). Compared to the C1s XPS spectrum of GO, that of GO-PVA exhibits a clear change in the peak position, which can be attributed to the addition of PVA (Figure S3). While the spectra of both materials contain a peak at a binding energy of 284.5 eV, corresponding to the graphitic carbon atoms of GO, the second peak in the GO-PVA spectrum (centered at 287 eV) is clearly shifted to a lower binding energy than that of GO (centered at 286.5 eV). In the GO spectrum, this second peak can be deconvoluted into five components corresponding to the oxygenated functional groups of GO, with the hydroxyl group at the lowest binding energy. Modification of the GO surface with PVA, which contains hydroxyl groups that have a similar binding energy (286.1 eV) to those of GO (285.9 eV) increases the overall hydroxyl content. As such, it is reasonable to expect the peak representing the combined oxygenated groups of GO to shift to a lower binding energy. This explains the shift in the oxygenated peak position of GO-PVA and confirms the adsorption of PVA on GO.

In addition to the differences in peak positions, the relative peak intensities are also noticeably different in GO and GO-PVA (Figure S3). The intensity of the oxygenated peak in GO (287 eV) is significantly greater than that of the peak corresponding to graphitic carbon atoms (284.5 eV). In contrast, the intensity of the oxygenated peak in GO-PVA (286.5 eV) is similar to that of the graphitic carbon peak, suggesting that addition of PVA decreases the oxygen to carbon (O:C) ratio in GO-PVA. This is reasonable as the synthesized GO monolayers have an O:C ratio of 0.66 (as determined by XPS survey scan), while pure PVA has an O:C ratio of 0.5. For the prepared GO-PVA nanolaminates, which contain GO and PVA in an approximate 1:1.5 weight ratio (based on the thickness and similar chemical composition of the two materials), an O:C ratio of 0.56 would be expected. In agreement with this prediction, the measured O:C ratio for the prepared GO-PVA nanolaminates is 0.61. Together with the XPS spectrum of GO-PVA, these data confirm that the PVA coverage detected by EELS is also present across the entire surface of GO-PVA nanolaminates.
Figure S3. C1s XPS spectra of GO and GO-PVA. Both the peak shape and position of the GO spectrum change upon addition of PVA, indicating the successful modification of GO.

S4. FFT patterns of GO monolayers and GO-PVA nanolaminates

A comparison of the fast Fourier transform (FFT) patterns (obtained from the HRTEM images) of GO and GO-PVA reveals no significant differences between these two materials (Figure S4b, c), showing that TEM analysis alone cannot distinguish between them. Due to the presence of graphitic domains in GO and GO-PVA, both materials exhibit a symmetric six-fold pattern similar to that of pristine graphene (Figure S4a). The blurring of this six-fold pattern is attributed to the severe breaking of lattice symmetry in the graphitic domains of GO and GO-PVA.

Figure S4. HRTEM images and fast Fourier transform (FFT) patterns of single-layer (a) graphene, (b) GO, and (c) GO-PVA. Both GO and GO-PVA exhibit graphitic domains dispersed throughout a continuous network of oxidized domains.
S5. Elastic and rupture-force analysis of membrane deflection results

To consistently fit AFM force-deflection curves obtained from different samples, a set of criteria was established for selecting the region of the curve to be fitted using the linear elastic, membrane deflection model. Based on these criteria, the first point of the fitted region is selected as the point at which the force in the AFM cantilever matches the average force measured as the tip approaches the membrane as shown in Figure S5a. This is the point where the force in the cantilever is zero post-membrane adhesion (i.e., after the cantilever straightens after snapping into the membrane), the adhesion and deflection forces are balanced, and the tip effective force is zero. This selection is reasonable because adhesive effects are eliminated from the fitting process and only loads applied directly on the membrane by the AFM tip are considered. The final point of the fitted region is chosen at first occurrence of non-linear behavior, as determined by manipulating the linear elastic, membrane deflection model to the form for large deflections (Figure S5b).

\[
\ln F = 3 \ln \delta + \ln \frac{Eh}{q^3 a^2} \quad (S1)
\]

Based on these two points, the force deflection-curves are then fitted to the linear elastic, membrane deflection model using an in-house MATLAB code (Version 2016, MathWorks).

**Figure S5.** Selection of region to be fitted based on linear elastic, membrane deflection model. (a) Selection of first point for fitting the AFM force-deflection curves. This point corresponds to the deflection value when the tip effective force, post-membrane adhesion (i.e., after the cantilever straightens after snapping into the membrane), matches the average value force measured during tip approach. (b) Selection of the last point for fitting the AFM force-deflection curves, when the experimental data deviate from the value of the slope given by Equation S1.

Figure S6 summarizes the results obtained by fitting the obtained AFM membrane deflection data, as described in the Methods section of the manuscript, for GO-PVA, PVA-GO-PVA, and PVA-GO-PVA nanolaminates. The elastic moduli of polymer-covered GO materials is lower than that
of GO and in agreement with the rule of mixtures (ROM),\textsuperscript{510} attributable to the significant volume fraction occupied by the soft PVA component.

The rule of mixture (ROM) formula is:

\[ E = E_{GO} \frac{t_{GO}}{t} + E_{PVA} \frac{t_{PVA}}{t} \quad (S2) \]

where we have assumed uniform PVA coverage. Literature values of \( E_{GO} = 220 \text{ GPa} \textsuperscript{511} \) and \( E_{PVA} \approx 300 \text{ MPa} \textsuperscript{512} \). The PVA thickness \( (t_{PVA}) \) is computed from the total thickness \( (t) \) obtained from AFM thickness measurements. For a total thickness of 2.5 nm, \( t_{PVA} = 2.5 \text{ nm} - t_{GO} = 1.70 \text{ nm} \), with \( t_{GO} = 0.80 \text{ nm} \). Using Equation S2, \( E = 82 \text{ GPa} \), which is slightly higher than the \( E \) obtained by fitting the AFM force-displacement data.

As all of the nanolaminate samples contained equivalent volume fractions of GO and PVA, it is reasonable to expect that their elastic moduli should remain constant under the ROM framework. In terms of the performed analysis, membrane-deflection theory is unable to model the experimental results as the number of layers in the system increases and the problem approaches plate bending theory. In this light, and given that PVA-GO-PVA bi-nanolaminates consist of 6 total material layers, we assume that membrane deflection theory still holds given: i) the low stiffness of PVA, i.e., the indentation is effectively over two stiff GO layers; and ii) the cubic nature of the force-deflection behavior measured experimentally, i.e., force-deflection is linear when plate bending is dominant.\textsuperscript{513} Given our assumptions, the 2D elastic modulus of PVA-GO-PVA bi-nanolaminates should follow the modulus scaling relation \( E_{2D,n} = nE_{2D} \), since the 2D modulus of a system containing \( n \) layers of 2D elastic modulus \( E_{2D} \) should be \( E_{2D,n} \). Interestingly, the highest pre-stresses measured herein for GO-PVA nanolaminates (0.06 GPa ± 0.03 GPa) are much lower than those previously found for GO (0.7 ± 0.3 GPa),\textsuperscript{514} suggesting that PVA can induce significant lattice relaxation within the GO sheets.

**Table S1.** Elastic moduli and pre-stress values obtained in 21 experiments based on linear elastic analysis from force-deflection curves.

<table>
<thead>
<tr>
<th>System</th>
<th>2D elastic modulus (N/m)</th>
<th>Modulus (GPa)</th>
<th>Pre-stress (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO\textsuperscript{514}</td>
<td>192 ± 21</td>
<td>256 ± 28</td>
<td>0.7 ± 0.3</td>
</tr>
<tr>
<td>GO-PVA</td>
<td>196 ± 28</td>
<td>78 ± 11</td>
<td>0.06 ± 0.03</td>
</tr>
<tr>
<td>PVA-GO-PVA Nanolaminate</td>
<td>196 ± 26</td>
<td>78 ± 10</td>
<td>0.03 ± 0.01</td>
</tr>
<tr>
<td>PVA-GO-PVA Bi-nanolaminate</td>
<td>365 ± 72</td>
<td>72 ± 14</td>
<td>0.02 ± 0.01</td>
</tr>
</tbody>
</table>
Figure S6. Elastic moduli and pre-stress values obtained from membrane-deflection experiments. (a-c) Elastic moduli as obtained from linear elastic fit for (a) GO-PVA nanolaminate, (b) PVA-GO-PVA nanolaminate, and (c) PVA-GO-PVA bi-nanolaminate samples. (d-f) Pre-stress values as obtained from linear elastic fit for (d) GO-PVA nanolaminate, (e) PVA-GO-PVA nanolaminate, and (f) PVA-GO-PVA bi-nanolaminate samples.

S6. Strain-rate sensitivity of molecular dynamics calculations

The dynamics of hydrogen bond reformation have been previously explored in the literature.\textsuperscript{15,16} Specifically, the bond-reformation velocity for hydrogen-bonded systems, which considers the time and distance over which hydrogen-bond-reforming processes occur, has been estimated to be between 0.025-125 m s\textsuperscript{-1}, with an average speed of 35.7 m s\textsuperscript{-1}. In this light, and to assess the role of strain-rate sensitivity in our study, we conducted MD tension simulations of GO-PVA, with a single PVA chain, to extract shear force/crack opening behavior using strain rates between $1 \times 10^9$ s\textsuperscript{-1} ($v = 1.5$ m s\textsuperscript{-1}) and $1 \times 10^{10}$ s\textsuperscript{-1} ($v = 150$ m s\textsuperscript{-1}), as shown in Figure S7. Our results clearly suggest there is no significant strain-rate dependence when the strain rate is below $1 \times 10^9$ s\textsuperscript{-1} ($v = 15$ m s\textsuperscript{-1}), which justifies the values and trends for the traction-crack opening utilized in our study.
Figure S7. Analysis of strain-rate sensitivity for traction–crack-opening behavior of GO-PVA nanolaminates. (a) Average traction observed during calculations for GO-PVA nanolaminates, as a function of pulling speed, i.e., strain rate. (b) Traction–crack-opening response for GO-PVA nanolaminates simulated in this study.

S7. Crack-bridging and load-transfer behaviors in GO-PVA nanolaminates

Intuitively, the extent of crack bridging from PVA chains will depend on the arrangement of the chains with respect to the crack propagation direction. For instance, if no PVA chains interact with both sides of a crack, no bridging will be observed. Conversely, when there is at least one PVA chain spanning over the crack, it is reasonable to expect bridging to occur, and the number of chains/segments in effect will influence the ability to dissipate energy in the entire system. This variability of polymer configurations along the crack front should manifest in experiments and MD simulations. Therefore, we conducted a sensitivity analysis in which we shifted the initial position of the crack while using the same initial polymer layer to vary the number of chains that were able to effectively bridge the crack (Figure S8a-c). To further increase the numbers of effective polymer chains, we also designed a configurationally biased system such that all PVA chains were able to effectively bridge cracks (Figure S8d). It is noted that due to the opening of the cracks, the chains seemingly rotate to approximately align with the crack extension direction. As expected, the traction–crack-opening behavior and calculated $G_f$ values were dependent on the initial configuration of the PVA chains with respect to the crack position. For instance, while Figure S8b shows slightly higher traction at the beginning, the system in Figure S8c can bridge over longer crack separations due to the polymer configuration. Figure S8d has both large average tractions and crack-bridging lengths, which demonstrates optimum load-bearing behavior indeed occurs with neatly arranged PVA configurations.

Furthermore, we identified various load-bearing mechanisms in different systems, as shown in Figure S9. PVA chains are able to fold over a crack (Figure S9a), providing more bridging segments of a given chain that can bear higher amount of load. We also observed local bundling of PVA chains (Figure S9b), increasing the effective width of a crack-bridging region. This behavior led to an increase in local traction due to effective load sharing between bundled PVA
chains. Remarkably, PVA chains that are pulled out from one end of a crack can still bridge the crack by forming directly interacting PVA chain networks (Figure S9c), which can significantly extend the effective crack-bridging length. Our simulations show a strong synergistic behavior between GO-PVA and PVA-PVA interactions to enhance load-bearing capability, and in turn toughen GO-PVA systems. The calculated fracture process zone (FPZ) sizes \( L_p \) (or \( c_f \)) are 92.4-131.75 nm long, depending on the system. These results show a strong correlation between the pull-out length of polymer chains and the FPZ size. Notably, in all cases, the FPZ is significantly larger than the size of the oxidized domains present in GO, implying the large-scale bridging behavior associated with this crack bridging mechanism.

\[
L_p = c_f = C \frac{w_{Tc}^2 E}{G_F} \approx 159\text{nm} \quad (S3)
\]

This process zone length is slightly larger than the one estimated by the FEM simulations, primarily due to the approximate nature of the computation of \( C \approx 0.032 \), which is based on the geometry of the double-cantilever beam.

**Figure S8.** 2D traction–crack-opening behavior for GO-PVA nanolaminates. (a-d) Traction–crack-opening curve and initial geometry for (a-c) systems with the same polymer layer but different initial crack position and (d) configurationally-biased GO-PVA system for optimal crack-bridging efficiency. The estimated energy-release rate value for each configuration, \( G_f \), is inset in the traction-separation curves.

Aside from FEM, the fracture process zone sizes can be roughly estimated from \( G_F, E \), and the critical crack-tip-opening displacement \( w_{Tc} \) based on the two-parameter fracture model discussed by Jenq and Shah\(^{S17}\). It should be noted that such a displacement should be taken at the location where the traction suddenly drops (Figure 4b). This feature was articulated by Bažant\(^{S18}\) who pointed out that the fracture process zone length \( (c_f) \), extracted from size effects, is independent of the tail. Hence, \( w_{Tc} = 17\text{ nm} \) and \( c_f \) is estimated to be:

\[
L_p = c_f = C \frac{w_{Tc}^2 E}{G_F} \approx 159\text{nm} \quad (S3)
\]
Figure S9. Summary of observed load-bearing mechanisms in GO-PVA nanolaminates. (a) PVA chains folded over the crack to form multiple bridging segments. (b) Local bundling of PVA chains bridging the crack (marked with red circles), increasing the local traction. (c) PVA chains form inter-connected bridges through interaction between different PVA chains, providing longer effective bridging lengths.

S8. Thickness of GO monolayers, nanolaminates, and bi-nanolaminates

Comparing AFM thickness measurements of GO monolayers before and after PVA modification revealed an increase in thickness, indicating the successful adsorption of PVA chains onto GO. Unmodified GO monolayers have a thickness of about 0.8-1 nm (Figure S10a), in good agreement with previous reports.\textsuperscript{20,21} After Langmuir-Blodgett deposition of an ultra-thin layer of PVA onto GO monolayers (see Methods section in the manuscript), the thickness of the resulting GO-PVA nanolaminates is around 2.5 nm (Figure S10b), suggesting that the layer of PVA on GO is about 1.5-1.7 nm thick. Compared to GO, the increased local height variations on the GO-PVA nanolaminate surface are attributed to the discontinuous microscale PVA network on GO, as discussed in the manuscript. In contrast, the local surface height of the PVA-GO-PVA nanolaminates is more uniform, despite having similar measured thickness as the GO-PVA nanolaminates (about 2.5 nm; Figure S10c, orange line). This is due to the difference in fabrication process: PVA-GO-PVA nanolaminates were produced by spin-coating a premixed solution of GO and PVA, rather than Langmuir-Blodgett deposition (see Methods section in the manuscript), which presumably results in more homogeneous PVA coverage at the microscale.
Figure S10. AFM characterization of GO monolayers and nanolaminate systems. (a) GO monolayer, with a height of ~1 nm. (b) GO-PVA nanolaminate, with a height of ~2.5 nm. The height variation of the nanolaminate is due to the microscale PVA network on the surface of GO. (c) PVA-GO-PVA nano- and bi-nanolaminates. PVA-GO-PVA nanolaminates on both Si (orange line) and another nanolaminate (green line) exhibit a height of ~2.5 nm; as such, the bi-nanolaminate is expected to have a thickness of ~5 nm.

In addition, an even-thinner PVA layer can be achieved by spin-coating a GO-PVA solution, as PVA chains adsorb to both faces of GO monolayers within the premixed solution. This implies that the PVA layer on each face is only about 0.75 nm thick. Therefore, bilayer PVA-GO-PVA nanolaminates comprising a stack of two PVA-GO-PVA nanolaminates should have a thickness of around 5 nm. As seen in Figure S10c (green line), the thickness of a PVA-GO-PVA nanolaminate stacked on top of another PVA-GO-PVA nanolaminate is about 2.5 nm, suggesting that the entire bilayer assembly does indeed have a thickness of around 5 nm. Together, these AFM measurements clearly show the presence of PVA on GO monolayers and confirm that the employed fabrication methods can achieve ultrathin (~0.75-1.7 nm) PVA layers on GO.

S9. Mechanistic implication of the membrane-deflection results

Due to the patchy nature of the GO monolayer membrane,²² (Figure S4) and also to the relatively disordered arrangement of PVA chains (that adsorb to such patchy surface), the responses of the membrane-deflection tests via tip-force-displacement curves show some variability. Indeed, this phenomenon is seen in Figure S11, where several force-displacement curves for the GO-PVA nanolaminates are plotted along with their corresponding fitted Young moduli and membrane pre-stress values (red curves). One common feature observed in all of the force-displacement plots is that after the onset of inelasticity (marked by the deviation from the fitted elastic response), the tip force further increases and reaches a peak load of ~150-200 nN. After a slight decrease, the tip forces on some membranes continue to experience further enhancement or levels off. Meanwhile, some samples exhibit a drop, indicating that the membranes are undergoing a more localized failure.
**Figure S11.** Set of AFM membrane-deflection results. Red lines indicate the best fit in the elastic regime of each sample, blue lines are the measured force-displacement curves.

Similar to the nano-indentation test, the circular-membrane-deflection test does not enable direct measurement of stress-strain material behavior.\textsuperscript{523} Hence, a constitutive model must be assumed in Finite Element Analysis (FEA) to correlate the experimental measurements to the mechanical properties of the membrane. With such a model, we aim to unravel the deformation and failure mechanisms and infer the mechanical behavior of the layers, separately and as a whole. In the FEA simulation, GO and PVA were modeled as layers with radii of 865 nm and 300 nm, respectively, using thin-shell elements.\textsuperscript{524} The indenter was modeled as a rigid solid with a tip radius of 25 nm. While the radius of the GO membrane was chosen to reflect the real membrane size, the size of PVA layer was decreased to reduce the computational cost. Because the focus of the simulation is to extract the role of PVA on toughening GO, which primarily occurs around the contact area, the dimensions of the PVA layer were chosen to be large enough to cover the nanolaminate region undergoing inelasticity and fracture. The cohesion between GO and PVA was then simulated as a surface-based (zero-thickness) cohesive law. The parameters for the cohesive law were estimated from a set of MD simulations similar to those discussed in Section S7 (adhesion energy = 0.3425 nN/nm, shear strength = 93 MPa, and power law (with exponent equal to 1) for mix-mode behavior). The GO constitutive law is based on our prior work.\textsuperscript{511,22}
PVA constitutive law can also, in principle, be extracted from reports in the literature, e.g., works by Chen et al. and Chee et al. These laws were based on ultra-thin layers of polymers in confined states and have a functional elasto-plastic form that captures the interaction of PVA chains relatively to each other (due to hydrogen-bond breaking and reforming). We will show next that such elasto-plastic law is not sufficient to describe the behavior of an ultra-thin PVA layer adhered to oxidized domains of GO. The behavior of the polymer layer appears to be quite complex due to confinement arising from the absorption of PVA on GO, local pressing of the indenter tip against a highly stretched membrane, and the evolving polymer-network configuration. To address this complexity, we explored four models for the absorbed PVA, starting with one that was reported in the literature followed by three simplified but physically motivated models.

**Figure S12.** Analysis of the membrane-deflection tests using different PVA constitutive laws. (a) PVA as an elasto-plastic membrane with $E = 5.2 \text{ GPa}$, $\sigma_f = 0.3 \text{ GPa}$, $H = 0 \text{ GPa}$, $\bar{\varepsilon}_{p,c} = 0.8$ (blue), $H = 1.2 \text{ GPa}$, $\bar{\varepsilon}_{p,c} = 0.8$ (red). (b) PVA as an elastic membrane with $E = 20 \text{ GPa}$ (blue), $E = 10 \text{ GPa}$ (red), $E = 5.2 \text{ GPa}$ (green), $E = 2 \text{ GPa}$ (magenta). (c) PVA as an elastic membrane with $E = 20 \text{ GPa}$ and possesses continuous (blue) and detached patches (red). The black solid curve indicates the response of the GO membrane and the black dashed curve the elastic fit. Maximum stresses (effective plastic strain for elasto-plastic case) in the PVA layer corresponding to the following points: $A = 1.364 \text{ GPa}$, $B = 1.737 \text{ GPa}$, $C = 1.044 \text{ GPa}$, $D = 1.318 \text{ GPa}$, $E = 0.712 \text{ GPa}$, $F = 0.887 \text{ GPa}$, $G = 0.438 \text{ GPa}$, $H = 0.547 \text{ GPa}$, $I = 0.0533 \text{ GPa}$, $J = 0.163 \text{ GPa}$ ($\bar{\varepsilon}_p = 0.0184$), $K = 0.163 \text{ GPa}$ ($\bar{\varepsilon}_p = 2.1564$), $L = 1.737 \text{ GPa}$, and $M = 0.794 \text{ GPa}$. 
The response of the membrane deflection, using the constitutive law extracted from PVA hydrogels (\(E \approx 5.2\) GPa, \(v = 0.4, \sigma_y \approx 300\) MPa, hardening modulus \(H = 0\) GPa, ultimate strain \(\epsilon_{p,c} \approx 0.8\)), is depicted as the blue curve in Figure S12a. Due to the sliding of the PVA chains, attributable to the breaking and reforming of hydrogen bonds, the elasto-plastic behavior without hardening leads to a deformation localization of the PVA into narrow regions following the fracture of GO under the indenter. As a result, the combined GO-PVA behavior is not consistent with the experimental force-displacement curves shown in Figure S11.

Next, an inverse analysis was utilized to infer the behavior of PVA such that the FEA model can reproduce the features observed in the experimental measurements. The first “inverse model” we employed is motivated by the findings reported in Shao and Keten,\(^{27}\) which revealed an enhancement in both hardening modulus \(H\) and yield strength \(\sigma_{y,c}\) when the polymer chains are in a nanoconfined state. Assuming that after yielding, stresses in PVA can continue to develop to a yield strength of \(\sigma_{y,c} \approx 1\) GPa at \(\epsilon_{p,c} = 0.8\), the red curve plotted in Figure S12a is obtained. This result illustrates that even for such a very-high yield strength, the elasto-plastic law fails to capture the observed phenomenon. Higher yield strengths just delay localization of the polymer deformation but do not capture the significant post-yield rising of the load as the deflection increases.

The second “inverse model,” is based on a polymer constitutive law with a fast-raising stress-strain behavior after initial yielding (in polymer networks this typically arises from cross-linking statistics and entropic effects). In the limit, this corresponds to a case where the backbone of the PVA chains is stretched within a polymer network subject to high indenter pressure. In the FEA model depicted in Figure S12b, these chains are bridging microcracks forming in the GO. For simplicity, we neglect the initial yield in our FEA model and directly account for the fast-raising stress-strain behavior, in this deformation regime, as a material stiffness to be identified via the inverse analysis. Values of \(E = 20, 10, 5.2,\) and 2 GPa, and a Poisson’s ratio equal to 0.4 were used in the simulations (Figure S12b). Although lower \(E\) values result in increasing compliance after the onset of GO damage, the curves show in general that such systems are relatively stiff, as observed by the limited deviation from the elastically fitted curve (dash line). While this model does not account for polymer failure and stresses within the membrane can reach unrealistically high values, it provides a good understanding of the stress-strain stiffening needed to capture the observed experimental behavior. We next augment the model to include a polymer-failure mechanism.

The third “inverse model” takes into account the finite length of the PVA chains while their constitutive law is represented by a linear-elastic behavior, consistent with the post-yielding fast-raising stress-strain behavior of the assumed polymer constitutive law. In this model, we represent the PVA membrane by discontinuous patches that would form upon membrane stretching (see Figs. S8 and S9), with dimensions that are consistent with the fully extended length of the PVA chains (\(\sim 33\) nm for a chain with molecular weight of 6 kDa). The model prediction is shown in Figure S12c (red curve). Even when a Young modulus of 20 GPa was used for the PVA, the compliance of the whole membrane after the GO layer was cracked increases with a significant deviation from the elastic fit (dash line), consistent with the experimental measurements. Due to discontinuities in the PVA layer, which arose from sliding chains and their finite size, the stresses in each patch could raise up to a maximum value, estimated as \(\sim 0.794\) GPa by the model. We note that this is in line with the equivalent 3D stress predicted by MD simulations of the crack-bridging process (see Figure S8). Subsequent sliding of the PVA patches increases the compliance of the whole system but the load, and hence the amount of energy dissipated by the system,
increases. Further sliding leads to a peak load and ultimately to membrane penetration by the indenter tip (Figure 5).

From the fact that the third “inverse model” best captures the experimental behavior of the nanolaminate, one can infer that the backbone strength of the ultra-thin PVA chains is being exploited via chain stretching and that chain sliding is controlled by the continuous breakage–reformation of H-bonds. This is consistent with the observation made in the discussion of the MD simulations, Section S7, and supports the assertion that the presence of PVA, with a single-chain thickness, is effectively toughening the GO layer.

S10. References