Fine-Tuned Ab Initio–Trained MACE Model for Predictive Mechanical Modeling of Graphene Oxide

Sara Shahbazi Fashtali[1], Guiseppe Zollo[1] (Arial 10)
[1]Dipartimento di Scienze di Base e Applicate per l'Ingegneria- Sapienza University of Rome, via A. Scarpa 14-16, Rome, 00161, Italy

Sara.shahbazifashtali@uniroma1.it

Abstract

Graphene oxide (GO) is a chemically heterogeneous two-dimensional material obtained through oxidation of graphite. Its structure depends strongly on oxidation level and the type and distribution of oxygen functional groups. Owing to its scalable production and combination of mechanical flexibility, tunable electronic structure, hydrophilicity, and biocompatibility, GO has attracted sustained interest in applications ranging from microelectronics to biomedical engineering. Variations in oxidation degree (typically 10–45%), together with the coexistence of sp^2 and sp^3 carbon domains, generate a highly complex atomic-scale network. The chemical heterogeneity directly governs the macroscopic mechanical response of GO, including stiffness, tensile strength, ductility, and fracture pathways. Because local bonding environments determine how strain is accommodated or localized, predictive modeling of GO mechanics requires an atomistic description capable of resolving competing oxygen configurations. However, establishing robust structure–property relationships remains challenging due to the limited transferability of empirical force fields and the computational cost of first-principles simulations [1-3].

Classical molecular dynamics with ReaxFF

Reactive force fields such as ReaxFF enable large-scale molecular dynamics simulations with dynamic bond breaking and formation, making them widely used for modeling GO under mechanical loading.
In our previous work [4], tensile stress–strain simulations were performed across oxidation levels of 10–45% and various hydroxyl-to-epoxy ratios. These simulations captured robust qualitative trends: increasing oxidation reduces Young's modulus and tensile strength due to disruption of the sp^2 carbon network, while ultimate strain exhibits a non-monotonic dependence with a maximum near ~30% oxidation. Functional-group chemistry also plays a role: hydroxyl-rich systems show higher stiffness, whereas epoxy-rich configurations display enhanced ductility associated with epoxy-to-ether transformations.

While these results demonstrate the capability of ReaxFF to capture chemically driven mechanical trends in GO, they also highlight important limitations. ReaxFF was originally parameterised for hydrocarbon combustion chemistry, rather than for the heterogeneous oxygen environments present in GO. As a result, its transferability to different oxidation contents and functional-group configurations is not guaranteed. Several studies report sensitivity of mechanical properties to the OH/O ratio, but without systematic or transferable trends across oxidation levels. We observe the same behaviour in our simulations: functional-group effects are clearly distinguished only at extreme OH/O ratios (pure epoxy or pure hydroxyl), whereas intermediate ratios exhibit ambiguous and non-systematic mechanical responses. This is particularly relevant for realistic GO, where hydroxyl groups dominate at higher oxidation levels but epoxides remain present; idealised models with only one functional group can therefore yield mechanically plausible but chemically unrealistic results. In addition, ReaxFF has been reported to overestimate tensile stresses in carbon-based systems, introducing further uncertainty in quantitative predictions. To overcome these limitations, we adopted a machine-learning interatomic potential trained directly on first-principles data.

MLIPs and MACE fine-tuning strategy

We employed a machine-learning interatomic potential (MLIPs) based on the MACE framework. Training data were generated in an iterative manner starting from the MACE-MP-0 foundation model, which was used to perform MD simulations of GO sheets at 10% and 20% oxidation with three functional-group configurations (OH/O = 1, epoxy-only, and hydroxyl-only). Each simulation included structural minimization, NPT equilibration, and NVT uniaxial tensile deformation, from which configurations were uniformly sampled along equilibrium and deformation pathways. Reference energies and forces for these snapshots were computed using density-functional theory (PBE functional, norm-conserving pseudopotentials, 90 Ry plane-wave cutoff, Γ-point sampling).
Several available MACE foundation models were benchmarked against this initial DFT dataset by comparing RMSEs in energies and forces, and MATPES-PBE was identified as the most accurate starting point. Fine-tuning was first performed using the DFT-labeled dataset obtained from GO-10% and GO-20% systems (993 training and 110 validation structures). In a second iteration, the dataset was expanded by adding DFT-labeled configurations from additional MD simulations of higher-oxidation systems (30% and 40%, OH/O = 1 and 3), again generated using MACE-MP-0, resulting in a total of 3318 training and 369 validation structures. The final fine-tuned MACE model achieves RMSEs of approximately 2.2 meV/atom in energy and 60–70 meV/Å in forces on validation data, while remaining stable during molecular-dynamics simulations under mechanical loading. Importantly, the subsequent large-scale validation systems were not included in the fine-tuning dataset, providing an explicit test of transferability.

Results: MACE vs ReaxFF MD

To evaluate transferability at realistic length scales, the fine-tuned MACE-MATPES-PBE potential was applied to GO sheets containing ~1500 atoms, spanning oxidation levels from 10% to 40% and hydroxyl-to-epoxy ratios ranging from epoxy-rich to

hydroxyl-rich regimes (OH/O ≈ 0–3) as well as pristine graphene. These larger systems were not included in the training dataset, enabling an explicit assessment of predictive performance. For each configuration, uniaxial tensile tests were performed under identical simulation conditions, and Young's modulus, ultimate tensile strength (UTS), and ultimate strain were extracted. Equivalent simulations were conducted using ReaxFF for direct comparison (Fig. 1).

The fine-tuned MACE potential exhibits a systematic oxidation-dependent mechanical response across all functional-group configurations. For OH/O = 1, both Young's modulus and UTS decrease nearly linearly with increasing oxidation, consistent with progressive disruption of the sp^2 carbon network and increasing sp^3 content. This scaling behavior remains coherent across different OH/O ratios, indicating that the model preserves the expected coupling between hybridization state and elastic stiffness. No artificial stiffening, plateau behavior, or anomalous stress enhancement is observed at intermediate oxidation levels.

In contrast, ReaxFF displays irregular scaling across oxidation regimes. Young's modulus remains nearly constant between 10–25% oxidation for several OH/O ratios and locally increases with additional oxygen content, contradicting the expected degradation of network connectivity. Similarly, UTS values in hydroxyl-rich systems remain unchanged or increase between 20–40% oxidation, indicating incorrect force redistribution under strain. These inconsistencies reveal limited transferability of the empirical parameterization to competing oxygen coordination environments.

Beyond macroscopic mechanical trends, the fine-tuned MACE model provides additional chemical insight into deformation pathways. While it does not constitute a fully first-principles fracture description, it resolves oxygen-specific bond rearrangements during tensile loading. In epoxy-rich systems, epoxy-to-ether transformations are observed prior to crack propagation, contributing to strain accommodation. In hydroxyl-rich configurations, bond weakening and local OH detachment occur at high strain and act as precursors to fracture. These chemically resolved events are either suppressed or inconsistently triggered in ReaxFF simulations, highlighting the improved representation of local oxygen chemistry in the ML-based framework.

Overall, the large-scale simulations demonstrate that the fine-tuned MACE potential provides chemically consistent, transferable, and deformation-stable predictions of GO mechanical properties, whereas ReaxFF exhibits oxidation- and functional-group–dependent artifacts that limit its predictive reliability.

References

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Figures

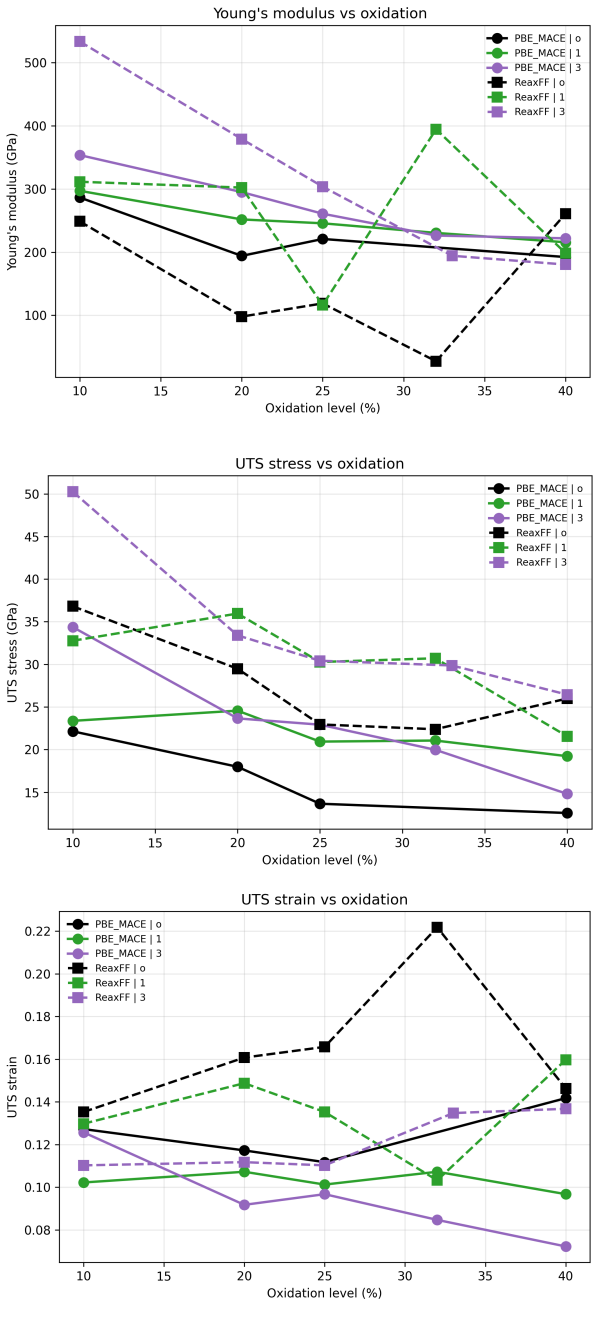

Figure 1. Oxidation-dependent mechanical properties of GO (a) Young's modulus, (b) ultimate tensile strength (UTS), and (c) ultimate strain as a function of oxidation level for representative (OH/O = 0, 1, 3).