



Thermomechanical insight into the stability of nanoporous graphene membranes

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ABSTRACT

Porous graphene (PG) is a graphene derivative endowed of nanoporous architectures. This material possesses a particular structure with interconnected networks of high pore volume, producing membranes with a large surface area. Experiments revealed that PG combines remarkable properties such as high mechanical strength and good thermal stability. In this work, we have carried out fully-atomistic reactive (ReaxFF) molecular dynamics simulations to perform a comprehensive study on the elastic properties, fracture mechanism, and thermal stability of 2D porous *n*-Benzo-CMPs (CMP and *n* refer, respectively, to π -conjugated microporous polymers and the pore diameter) membranes with distinct nanoporous architectures. For comparison purposes, the results were also contrasted with the ones for graphene sheets of similar dimensions. We adopted three different nanoporous diameters: small (3.45 Å), medium (8.07 Å), and large (11.93 Å). Results showed that PG is thermally stable up to 4660 K, about 1000 K smaller than the graphene melting point (5643 K). During the PG heating, linear atomic chains are formed combining carbon and hydrogen atoms. The fracture strains range between 15% and 34% by applying a uniaxial loading in both plane directions for temperatures up to 1200 K. The fracture strain increases proportionally with the nanoporous size. All the PG membranes go abruptly from elastic to completely fractured regimes after a critical strain threshold.

1. Introduction

Porous Graphene (PG) membranes are graphene-related materials composed of a large surface area containing nanopores with different shapes and sizes [1,2]. PG membranes are interesting materials due to their low density and high strength, being capable of bonding with other atoms through their sp , sp^2 , and sp^3 hybrid orbitals [3,4]. They have emerged to overcome the problem of the severely reduced surface area presented by graphene layers when in contact, which heavily weakens several of their outstanding properties [5]. In this sense, the surface area of graphene — or assembly of graphene layers — is enlarged by tailoring the lattice morphology via pore production [6]. PG membranes have been employed to develop several applications, ranging from biomedical [7,8] to energy storage and conversion devices [9–13]. To further explore the functionalities of PG, many studies have been devoted to designing novel advanced PG-based materials with both 2D and 3D architectures and endowed of more accessible electroactive areas [14–16].

PG membranes present a random or high regularity distribution of nanoporous [17]. These pores are classified according their diameters

(D) as: micropores ($D < 2$ nm), mesopores ($2 \text{ nm} < D < 50$ nm), and macropores ($D > 50$ nm) [18]. To produce them, some sp^2 carbon atoms are removed from the pristine graphene lattice. Particularly, PG layers with micropores are employed in developing new technologies for water and air purification, due to its spongy structure [19]. The ones displaying mesopores and macropores, in turn, have been used as active layers in electrochemical capacitors [20]. Among all the species of 2D porous graphitic materials, *n*-Benzo-CMPs (where CMP and *n* refer, respectively, to π -conjugated microporous polymers and the pore size), stand out due to their direct semiconducting bandgaps (0.6–1.75 eV), making them interesting for a wide range of optoelectronic applications [21]. Importantly, their synthesis has revealed novel functions for potential applications as super-capacitor in the energy storage or electric power supply [22].

Recently, several theoretical studies were performed inspired by the successful synthesis of 2D porous CMPs [21,23–29]. The electronic and transport properties of *n*-Benzo-CMPs and BN codoped derivatives were investigated using density-functional theory (DFT) and the non-equilibrium Green's function methods [21]. The results showed that these materials possess interesting structural, electronic, and transport

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properties that are notably different from those of the graphene. Their direct semiconducting bandgaps ranged from 0.19 to 2.0 eV depending on the pore size diameter, which has varied within the interval 3.68–12.93 Å, and the doping degree, in the sense that BN codoping tends to reduce the bandgaps [21]. Molecular dynamics (MD) simulations were performed to study the gas separation performance of PG membranes with H-passivated nanopores [23–25,29,27]. Some models of PG systems with different sizes and shape were designed to obtain an efficient CO₂/H₂ [23] and CO₂/N₂ [25] separation. MD simulation results showed that H-passivated membranes with a pore size of 3.75 Å perform high selectivity and desirable permeability for CO₂/H₂ separation while smaller and larger pores demonstrated less permeability and selectivity, respectively [23]. Moreover, it was reported in reference [25] that H-passivated membranes with a pore size of 4.06 Å can efficiently separate N₂ from CO₂. This particular PG membrane exhibited high N₂ selectivity over CO₂, with an N₂ permeance of 105 GPU (gas permeation unit) [25]. No CO₂ was found to pass through the pore. The main conclusion in both studies is that the electrostatic sieving plays a fundamental role in hindering the passage of CO₂ molecules through the pore [25]. As mentioned above, PG membranes have been successively employed to develop a wide range of applications. Nevertheless, some intrinsic thermomechanical properties of these materials, that may impact their performance in these applications, remain not described and further investigations are needed to fill this gap.

In the present work, the mechanical and thermal stability of microporous 2D *n*-Benzo-CMPs membranes were systematically investigated in the scope of fully-atomistic reactive (ReaxFF) molecular dynamics simulations. We have considered three different H-passivated nanoporous diameters: small (3.45 Å), medium (8.07 Å), and large (11.93 Å). A heating ramp protocol was applied to obtain the melting point for the PG membranes. Their mechanical behavior was studied using the stress–strain relationship and fracture toughness.

2. Methodology

The mechanical and thermal properties of microporous 2D *n*-Benzo-CMPs membranes were studied through MD simulations using the reactive force field ReaxFF potential [30,31], as implemented in the large-scale atomic/molecular massively parallel simulator (LAMMPS) code [32]. As expected in reactive potentials, the ReaxFF force field allows the formation and breaking of chemical bonds during the dynamics, which is useful to investigate the PG fracture mechanism. The studied H-passivated PG membranes are illustrated in Fig. 1. In this figure, it is depicted in the left-most panels the 3.45-Benzo-CMP (System – S, with 06 hydrogens in the pore), in the middle panels the 8.07-Benzo-CMP (System – M, with 12 hydrogens in the pore), and in the right-most panels the 11.93-Benzo-CMP (System – L, with 18 hydrogens in the pore). In Fig. 1, the carbon and hydrogen atoms are represented by the gray and white spheres, respectively. The system dimensions are: 102.13 × 100.81 Å² (System – S, 3024 carbons and 1008 hydrogens), 109.5 × 100.9 Å² (System – M, 2400 carbons and 960 hydrogens), and 116.87 × 100.79 Å² (System – L, 2016 carbons and 864 hydrogens). It is worthwhile to stress that the systems were built in order to obtain 2D membranes with dimensions of about 100 × 100 Å², preserving the periodic boundary conditions.

The equations of motion were numerically integrated using the velocity-Verlet integrator with a time-step of 0.05 fs. We increased the tensile stress in the system by applying a uniaxial strain along the periodic *x* and *y* directions, for an engineering strain rate of 1.0 × 10^{−6} fs^{−1}. It is worthwhile to stress that the effect of time step and strain rate on ReaxFF simulations of mechanical failure in graphene was investigated recently [33]. The results showed that MD time steps of 1.0 fs or larger resulted in inaccurate predictions of material failure, whereas step sizes of 0.5 fs and smaller were shown to predict physically realistic mechanical responses. Moreover, the findings have also

revealed that strain rate effects were not observed for strain rates below 2.2 × 10^{−6} fs^{−1}. The PG membranes were stressed up to their complete rupture, which is identified by the fractured and irreversible patterns presented by the systems when separated into two moieties. To eliminate any initial stress within the membranes, before the stretching procedure they were equilibrated/thermalized within an NPT/NVT ensembles at constant temperatures (300 K, 600 K, 900 K, and 1200 K) and null pressures using the Nosé-Hoover thermostat [34,35] during 100 ps. Within this MD simulation protocol, Young's modulus (*Y*), Fracture Strain (*FS*), and Ultimate Strength (*US*) are the elastic properties derived from the stress–strain curves obtained for each temperature considered here.

To better analyze the outcomes from the stretching dynamics, we calculated the von Mises stress (VM) per-atom values [36]. The VM values provide useful local structural information on the fracture mechanism, once they can determine the region from which the structure has started to yield the fractured lattice. In this way, the VM equation can be written as

$$\sigma_v^k = \sqrt{\frac{(\sigma_{xx}^k - \sigma_{yy}^k)^2 + (\sigma_{yy}^k - \sigma_{zz}^k)^2 + (\sigma_{xx}^k - \sigma_{zz}^k)^2 + 6((\sigma_{xy}^k)^2 + (\sigma_{yz}^k)^2 + (\sigma_{zx}^k)^2)}{2}}, \quad (1)$$

where σ_{xx}^k , σ_{yy}^k , and σ_{zz}^k are the components of the normal stress and σ_{xy}^k , σ_{yz}^k , and σ_{zx}^k are the components of the shear stress. The MD snapshots and trajectories were obtained by using free visualization and analysis software VMD [37].

3. Results

We begin our discussions by analyzing the thermal stability of the microporous 2D *n*-Benzo-CMPs systems studied here. Fig. 2 shows representative MD snapshots for the heating ramp simulations (melting process), with temperature varying from 300 K up to 6000 K. In this figure, the columns present the lattice configurations for each kind of PG membrane at different temperatures, which increase from left to right. The color scheme denotes the temperature per-atom ranging from 300 K to 5000 K, which are represented by the blue and red colors, respectively. At low temperatures (300 K), the PG membranes present lattice configurations very close to their ground state arrangement. For temperatures about 3000 K, the thermal fluctuations lead the membranes to wrinkle due to large displacements presented by the atoms. Even so, the PG membranes keep their integrity. Above 4500 K, the 2D π -conjugated polymer arrangement showed by these PG membranes favors the formation of very short and linear atomic chains (LACs), which randomly combine carbon and hydrogen atoms during the melting process. Importantly, the wrinkling effect also favors LACs formation. For temperatures about 6000 K, only isolated atoms and small chain fragments that connect 2–10 atoms are observed. In this sense, the final morphologies obtained at the end of the melting process resemble a gas-like phase of carbon atoms.

Fig. 3 depicts the total energy (3(a)) and the heat capacity (C_V , 3(b)) as a function of temperature for the MD simulations presented in Fig. 2. For the sake of comparison, these quantities for a graphene membrane of similar dimensions are also presented. In Fig. 3(a), one can note that the total energy increases linearly with temperature by showing two well-defined regimes with different slopes for all the systems. The curves are almost parallel (for the porous graphene membranes) and the total energy slightly increases by increasing the nanopore diameter. Moreover, we can see a clear discontinuity in these curves that denotes a phase transition from a solid to a gas-like phase. This abrupt change in the slope of the curves is related to a gain in kinetic energy due to the higher atom velocities in the gas-like phase, which increases the total energy. A considerable part of the harmonic and torsional energies present in the solid phase is converted into kinetic energy, increasing the amount of such a contribution for total energy. For the microporous

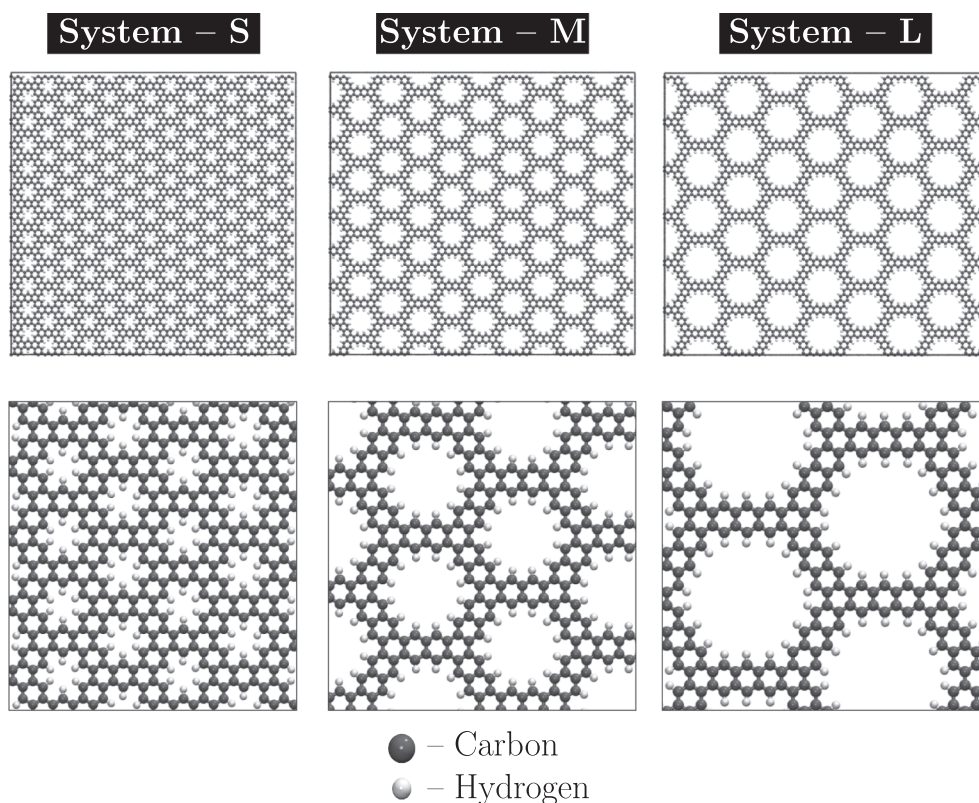


Fig. 1. Schematic representation of the microporous 2D *n*-Benzo-CMPs systems (porous graphene membranes) studied here. (a) 3.45-Benzo-CMP (System – S, 06 hydrogens in the pore), (b) 8.07-Benzo-CMP (System – M, 12 hydrogens in the pore), and 11.93-Benzo-CMP (System – L, 18 hydrogens in the pore). The carbon and hydrogen atoms are represented by the gray and white spheres, respectively. The system dimensions are: $102.13 \times 100.81 \text{ \AA}^2$ (System – S, 3024 carbons and 1008 hydrogens), $109.5 \times 100.9 \text{ \AA}^2$ (System – M, 2400 carbons and 960 hydrogens), and $116.87 \times 100.79 \text{ \AA}^2$ (System – L, 2016 carbons and 864 hydrogens).

2D *n*-Benzo-CMPs systems considered here, the temperatures for the phase transitions occur at 4660.07 K, 4574.36 K, and 4402.91 K, for the systems S, M, and L, respectively. For the graphene case, the transition from a solid to a gas-like phase occurs at 5595.09 K, which suggests that graphene membranes are more stable structures than the microporous 2D *n*-Benzo-CMPs. Importantly, previous atomistic MD and DFT

simulations have predicted a melting point for graphene about 5000–5700 K (about 1% higher) [38–43]. As expected, when it comes to thermal stability, our results suggest that PG membranes with small nanopore diameters resemble more a graphene sheet than the ones with large nanopore diameters. In Fig. 3(b), the C_V peaks (dashed lines) correspond precisely to the melting point of the PG membranes

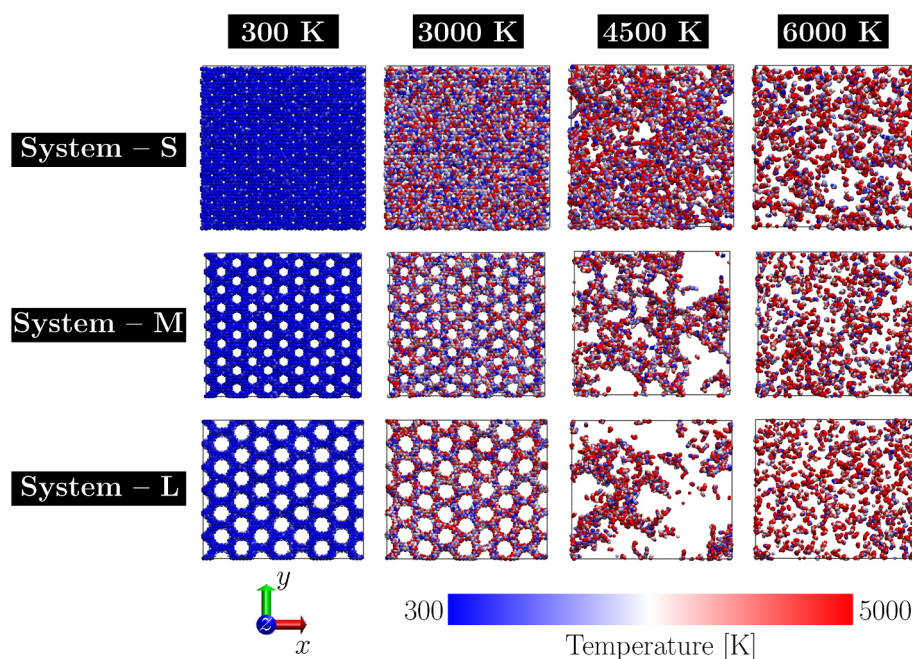


Fig. 2. Representative MD snapshots for the heating ramp simulations (melting process), with temperature varying from 300 K up to 6000 K for all the microporous 2D *n*-Benzo-CMPs systems studied here. The color scheme denotes the temperature per atom ranging from 300 K to 5000 K, which is presented by the blue and red colors, respectively.

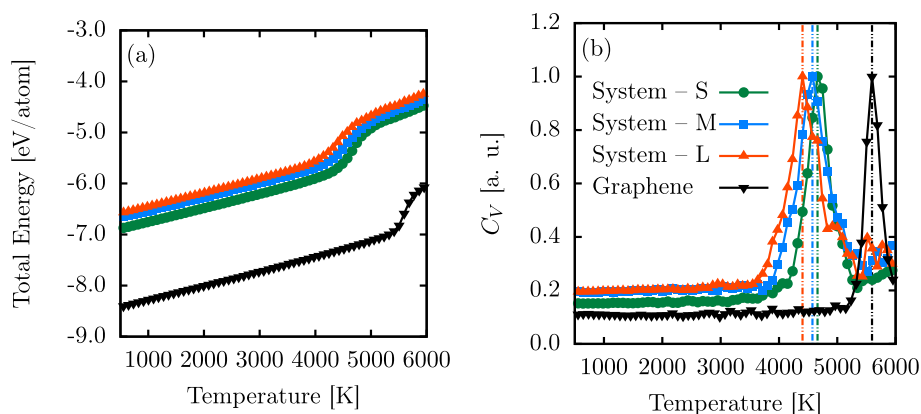


Fig. 3. (a) Total energy and (b) heat capacity (C_V) as a function of temperature for the MD simulations are presented in Fig. 2. In panel (b), the C_V peaks (dashed lines) correspond precisely to the melting points 5595.09 K, 4660.07 K, 4574.36 K, and 4402.91 K, for Graphene, System - S, System - M, and System - L, respectively.

(mentioned above). This figure helps to realize that the critical temperature for a particular PG membrane (System-L) is about 935 K smaller than the graphene melting temperature, also pointing to the good thermal stability of these PG membranes species.

Now, we discuss the mechanical behavior of PG membranes under uniaxial (x-direction) tensile loading. Fig. 4 shows representative MD snapshots for strain simulations at 300 K. In this figure, four different strain stages are illustrated for each system considered here. The color scheme refers to the minimum (blue) and maximum (red) VM stress values according to Eq. 1. For the sake of convenience, here we not present the MD snapshots in which the strain was applied in the y-direction since they are similar to the ones for the x-direction. With a rapid glimpse of Fig. 4, we can note that all PG membranes present similar elastic behavior and fracture pattern. These membranes have just one stage of elastic deformation and the critical strain increases proportionally with the nanopore diameter from 22.33% up to 33.74%. After these strain thresholds, the PG membranes go abruptly from elastic to a completely fractured regime, which is characteristic of a brittle behavior. The larger is the nanopore diameter the greater is the tendency of a PG membrane in collapsing on parallel conjugated polymer chains during the stretching process. This trend contributes to

diminish substantially the size of the membranes in the unstretched direction. The VM stress is uniformly distributed/accumulated on the membranes and for high values, it results in an abrupt rupture and fast crack propagation. The VM stress — or equivalently the potential energy gain — is stored in the carbon-carbon bonds almost parallel to the applied strain. Importantly, these bonds are the first to break, and two separated/unstressed pieces of PG lattices are obtained subsequently the membranes rupture. Other reactive MD simulations in the literature carried out using the ReaxFF [44] and AIREBO [38] potentials have shown that graphene sheets present a similar fracture process for a uniaxial stretching.

Finally, we present in Fig. 5 the calculated stress-strain curves for all PG membranes when subjected to temperature regimes ranging from 300 K to 1200 K, considering a uniaxial strain applied in both x and y directions. As can it be perceived, the membranes were stretched at a constant rate until total rupture. The stress-strain curves shown the common regions that take place when nanostructures are stressed [45]: (I) a quasi-linear elastic regime is observed up to a maximum stress value (the ultimate strength (US)), (II) then the stress value drops abruptly to zero (or close to it) when the PG membranes start to fracture until they ultimately break (III) for a critical fracture strain (FS). The US

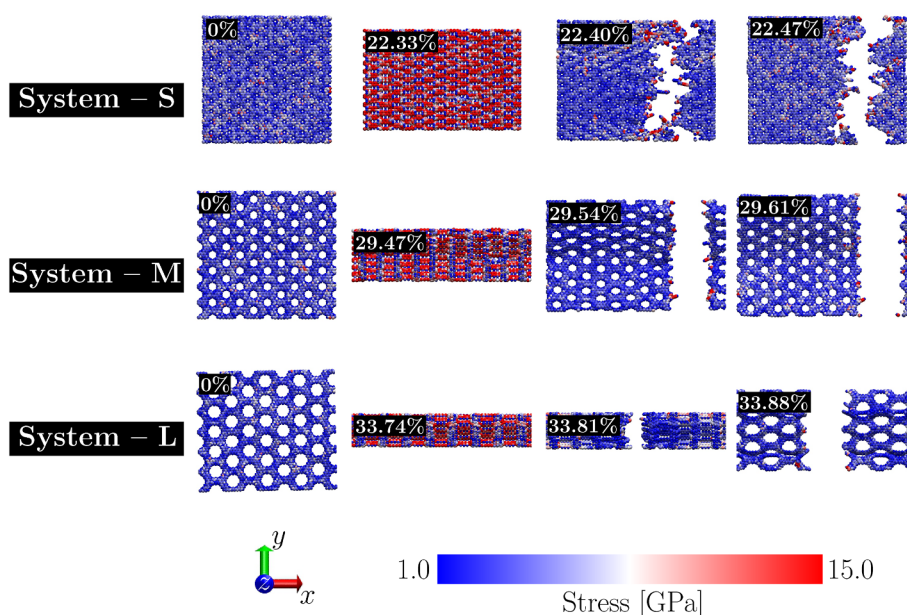


Fig. 4. Representative MD snapshots of the strain simulations at 300 K for all the microporous 2D *n*-Benzo-CMPs systems studied here. The color scheme refers to the minimum (blue) and maximum (red) VM stress values according to Eq. 1.

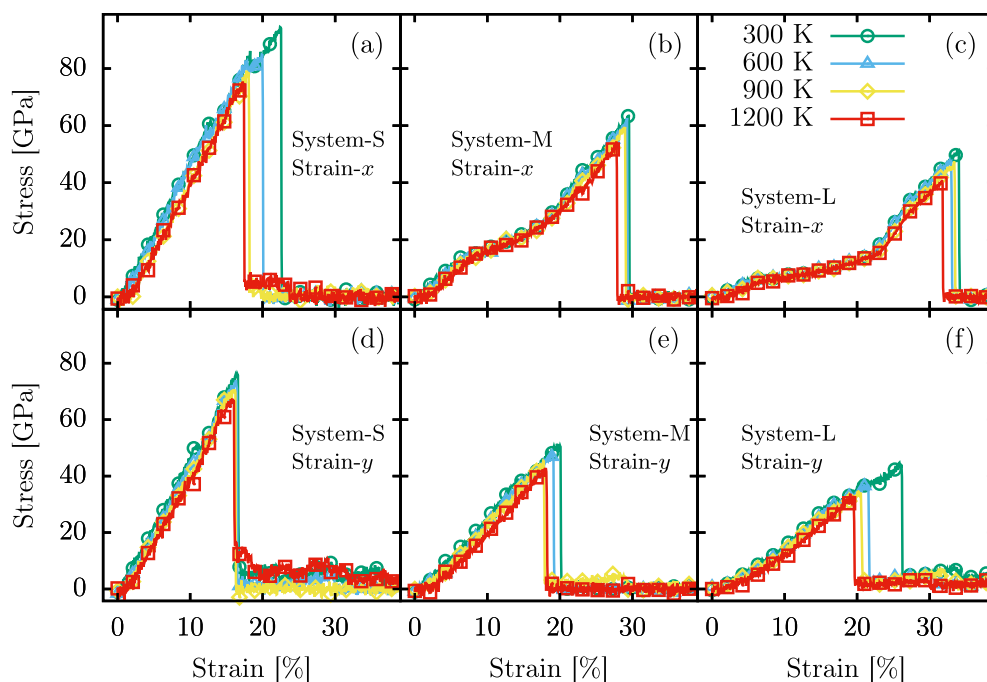


Fig. 5. Calculated stress–strain curves for all the PG membranes when subjected to temperature regimes ranging from 300 K to 1200 K, considering a uniaxial strain applied in both x and y directions. The membranes were stretched at a constant rate until total rupture.

Table 1

Elastic properties — Young's Modulus (Y_M), Fracture Strain (FS), and Ultimate Strength (US) — obtained by fitting the stress–strain curves (Fig. 5) for the n -Benzo-CMPs cases investigated here.

Temperature [K]	System-S					
	Strain-x			Strain-y		
	Y_M [GPa]	FS [%]	US [GPa]	Y_M [GPa]	FS [%]	US [GPa]
300	471.01	22.40	94.50	460.07	16.66	76.28
600	451.69	19.88	84.86	428.55	16.31	73.98
900	350.16	17.78	79.24	396.75	16.03	70.71
1200	339.17	17.22	75.41	369.35	15.82	67.43
Temperature [K]	System-M					
	Strain-x			Strain-y		
	Y_M [GPa]	FS [%]	US [GPa]	Y_M [GPa]	FS [%]	US [GPa]
300	236.04	29.47	63.40	239.44	19.60	51.42
600	220.76	29.26	62.62	208.17	18.83	48.12
900	183.66	28.84	59.56	190.05	17.71	45.39
1200	160.49	27.79	54.40	131.33	18.01	42.82
Temperature [K]	System-L					
	Strain-x			Strain-y		
	Y_M [GPa]	FS [%]	US [GPa]	Y_M [GPa]	FS [%]	US [GPa]
300	125.36	33.81	51.57	137.31	25.83	25.74
600	115.06	32.76	47.82	122.61	20.93	37.12
900	97.55	33.39	47.44	95.28	20.16	34.56
1200	81.65	31.71	40.59	80.36	19.04	33.73

values are slightly higher for the strain in the x -direction. This trend occurs since the bond angle variations in x - and y -direction are different and they govern the fracture strain, as discussed in literature [46,47]. In Fig. 5 one can note that the fracture strains range between 15%–34% by applying a uniaxial loading in both plane directions for temperatures up to 1200 K. The lowest fracture strain was obtained for

System-L at 1200 K (15.82%). As expected, increasing the temperature to 1200 K, there is a decrease in the critical tensile strain values for all PG membranes (see 1). Moreover, the highest Young's Modulus (Y_M) was obtained for System-S at 300 K (471.01 GPa). As also expected, these results indicate that the n -Benzo-CMPs with small nanopore diameters are stiffer than the ones with large pores, which is denoted by

the higher Y_M as well as lower FS values presented by System-L when contrasted to the other cases simulated here. Importantly, Table 1 summarizes the elastic properties (Y_M , FS , and US) that were obtained by fitting the stress-strain curves for the n -Benzo-CMPs cases investigated here.

4. Conclusions

In summary, we have performed fully-atomistic reactive (ReaxFF) molecular dynamics simulations to investigate the elastic properties, fracture mechanism, and thermal stability of 2D porous n -Benzo-CMPs membranes with distinct nanopore architectures. For the sake of comparison, the results were contrasted with the ones for graphene sheets of similar dimensions. We have considered three different H-passivated nanoporous diameters: small (3.45 Å), medium (8.07 Å), and large (11.93 Å). At low temperatures (300 K), the PG membranes present lattice configurations very close to their ground state arrangement. For temperatures about 3000 K, PG membranes keep their integrity. However, thermal fluctuations lead these membranes to wrinkle due to large displacements presented by the atoms. Above 4500 K, the PG membranes start to melt and their 2D π -conjugated polymer arrangement favors the formation of very short and linear atomic chains, which randomly combine carbon and hydrogen atoms. The initial configuration of the PG membranes vanishes completely for temperatures about 6000 K, where only isolated atoms and small chain fragments that connect 2–10 atoms are observed resembling a gas-like phase of carbon atoms. For the microporous 2D n -Benzo-CMPs systems considered here, the melting points occur at 4660.07 K, 4574.36 K, and 4402.91 K, for the systems S, M, and L, respectively. For the graphene case, the melting point occurs at 5595.09 K, which suggests that graphene membranes are more stable structures than the microporous 2D n -Benzo-CMPs. Previous atomistic MD and DFT simulations have predicted a melting point for graphene about 5000–5700 K [38,40,39].

Accurate measurements of the melting point of graphite shown experimental values ranging from 4000 K up to 5000 K [40]. Assuming graphene behaves thermomechanically like graphite, graphene should sublime at low pressure according to carbon's phase diagram which places the triple point of graphite around 4700 K [48–52]. This assumption is not so rough once recent experimental results showed that a graphene sheet has the in- and out-of-plane stiffness very similar to graphite [53]. In this way, such an overestimation obtained in the present study for the sublimation temperature of 2D porous -Benzo-CMPs and graphene membranes one means that most probably ReaxFF and AIREBO potentials fail to describe melting and sublimation processes in carbon-based nanomaterials. Therefore, further corrections on both models are required to obtain the genuine melting temperature of this particular class of materials.

The PG membranes under uniaxial tensile loading have presented similar elastic behavior and fracture pattern. They have just one stage of elastic deformation and the critical strain increases proportionally with the nanopore diameter from 22.33% up to 33.74%. After these critical strain values, the PG membranes go abruptly from elastic to a completely fractured regime. During the stretching process, the stress was uniformly accumulated on the membranes and for high values, it results in an abrupt rupture and fast crack propagation. The US values are slightly higher for the strain in the x -direction. This trend occurs since the bond angle variations in x - and y -direction are different and they govern the fracture strain. The lowest fracture strain was obtained for System-L at 1200 K (15.82%). As expected, increasing the temperature to 1200 K, there is a decrease in the critical tensile strain values for all PG membranes. The highest Young's Modulus (Y_M) was obtained for System-S at 300 K (471.01 GPa).

CRedit authorship contribution statement

Marcelo Lopes Pereira Júnior: Writing - original draft. Luiz

Antônio Ribeiro Júnior: Conceptualization, Supervision, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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