Thermal Stability and Fracture Patterns of a Recently Synthesized Monolayer Fullerene Network: A Reactive Molecular Dynamics Study

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Abstract: New monolayer 2D carbon structures, namely qHPC60 and qTPC60, were recently synthesized by covalently bonding C60 polymers. Here, we carried out Reactive (ReaxFF) molecular dynamics simulations to study the thermodynamic stability and fracture patterns of qHPC60 and qTPC60. Our results showed that these structures present similar thermal stability, with sublimation points of 3898 K and 3965 K, respectively. qHPC60 and qTPC60 undergo an abrupt structural transition becoming totally fractured after a critical strain threshold. The crack propagation is linear (non-linear) for qHPC60 (qTPC60). The estimated elastic modulus for qHPC60 and qTPC60 are 175.9 GPa and 100.7 GPa, respectively.

1 Introduction

Since the discovery of graphene [1], 2D carbon materials have been widely studied to develop new optoelectronic applications [2]. Their controllable synthesis can yield different structures with distinct physical and chemical properties [3, 4]. Due to this reason, the large variety of 2D carbon allotropes proposed so far [5–14] have proven to be suitable for flat electronics, although only a few structures has been experimentally realized.

Recently, new 2D carbon allotropes were synthesised: the monolayer amorphous carbon (MAC) [11] and the 2D biphenylene network (BPN) [12]. MAC is made of randomly distributed five, six, seven, and eight atom rings. BPN consists of a periodic lattice composed of fused rings containing four, six, and eight carbon atoms. Similar to graphene, MAC and BPN present a zero semi-metal bandgap, which is a serious drawback to their usage in some optoelectronic applications [15].

Very recently, 2D carbon materials with a semiconducting bandgap of about 1.6 eV — namely monolayer quasi-hexagonal-phase fullerene (qHPC60) and monolayer quasi-tetragonal-phase fullerene qTPC60) — were experimentally realized overcoming the problem of a null bandgap shown by other 2D carbon-based materials [16]. It was reported that qHPC60 and qTPC60 show excellent environmental and thermal stabilities. The Raman spectra and optical images remain unchanged after heating, indicating that the polymeric C60 frameworks do not decompose up to 600 K. qHPC60 and qTPC60 exhibit high crystallinity and unique topological structure [16]. In this sense, a detailed description of their structural integrity with a focus on thermodynamic stability and stress resilience can pave the way for its applications.

In the present work, we investigated the thermodynamic stability and stress resilience of qHPC60 and qTPC60. It was observed that these materials present a well-defined (linear) elastic
region when subjected to uniaxial strain. \(q\text{HPC}_{60}\) and \(q\text{TPC}_{60}\) undergo an abrupt structural transition to a totally fractured form after a critical strain threshold. The crack propagation is linear for \(q\text{HPC}_{60}\) and non-linear for \(q\text{TPC}_{60}\), respectively. Heating ramp protocol simulations revealed that they are thermally stable up to 3898K and 3965K, respectively.

2 Methodology

We carried out fully-atomistic MD simulations with the reactive force field ReaxFF (by employing the parameter set for C/H/O [17, 18]), as implemented in LAMMPS [19]. A reactive potential is needed (it allows the formation and breaking of chemical bonds during the dynamics) for the fracture dynamics investigation. Figure 1 illustrates the \(q\text{HPC}_{60}\) and \(q\text{TPC}_{60}\) structural models (supercells) used in the MD simulations. Both structures have dimensions of \(100 \times 100 \text{ Å}^2\) with periodic boundary conditions and are composed of 8640 atoms. The length of the simulation box along the z-direction is 200 Å.

![Figure 1: Schematic representation of: (a) \(q\text{HPC}_{60}\) and (b) \(q\text{TPC}_{60}\) lattice structures. The right panels illustrate the corresponding unit cells.](image)

The equations of motion were numerically integrated using the velocity-Verlet algorithm, with a time-step of 0.2 fs. The uniaxial tensile strain was applied along the periodic x and y directions, for an engineering strain rate of \(1.0 \times 10^{-6} \text{ fs}^{-1}\). Before their heating and stretching, the structures were equilibrated using an NPT ensemble at a constant temperature of 300 K and null pressures using a Nosé-Hoover thermostat [20] during 200 ps.

To obtain the mechanical properties and fracture patterns, the \(q\text{HPC}_{60}\) and \(q\text{TPC}_{60}\) structures were continuously stretched up to their complete structural failure (fracture) by applying a maximum strain of 50%. The tensile stretching simulations were performed by increasing the x and y cell dimensions. Their thermal stability was investigated by heating up the structures from 300K...
up to 10000K. The heating process is simulated by linearly increasing the temperature during 1 ns in an NVT ensemble. The MD snapshots and trajectories were obtained using the visualization and analysis software VMD [21].

3 Results

We begin our discussion by analyzing the qHPC$_{60}$ and qTPC$_{60}$ thermodynamic stability. The melting processes occur within the heating ramp simulations, as mentioned above. Figure 3 illustrates the total energy (green) and heat capacity ($C_V$, in yellow) as a function of temperature for the melting process of qHPC$_{60}$ (Figure 2(a)) and qTPC$_{60}$ (Figure 2(b)). As a general trend, we can see that the total energy increases quasi-linearly with the temperature showing three different slopes: between 300K-3500K, 3500K-4000K, and 4000K-10000K.

![Figure 2: Total energy and heat capacity ($C_V$) as a function of temperature for: (a) qHPC$_{60}$ and (b) qTPC$_{60}$ at 1 ns of the heating ramp simulations.](image)

qHPC$_{60}$ and qTPC$_{60}$ maintain their structural integrity in the first stage of the heating process, defined by temperatures up to 3500K. After this critical value, the thermal vibrations impose substantial changes in their morphologies, and the melting process occurs in the second stage of the heating process (for temperatures ranging from 3500K up to 4500K). The melting point is defined by the most pronounced peak in the $C_V$ curves. In this sense, the peak in the heat capacity curve indicates the similar melting points at 3898K (see Figure 2(a)) and 3965K (see Figure 2(b)) for qHPC$_{60}$ and qTPC$_{60}$, respectively.

The third stage of the heating process (between 4000K-10000K) in Figures 2(a) and 2(b) characterizes the continuous heating of the systems. The abrupt change in the slope for the total energy curves defines a phase transition from a solid to a gas-like phase (sublimation) of the carbon atoms. The melting points obtained here for qHPC$_{60}$ and qTPC$_{60}$ are comparable to those for the monolayer graphene (4095K) [22], MAC (3626K) [23], and BPN (4024K) [24].

We further explored the thermodynamic stability of qHPC$_{60}$ and qTPC$_{60}$ by analyzing the representative MD snapshots for the heating ramp simulations, with temperatures varying from 300K up to 4000K, as shown in Figure 3. Figures 2(a) and 2(e) illustrate the lattice structure for qHPC$_{60}$ and qTPC$_{60}$ at 0K, respectively. In Figures 2(b-c) and 2(f-g), we can note the melting process of these structures occurs differently. For the qHPC$_{60}$, the C$_{60}$ units are fragmented into several linear atomic chains (LACs) at 1600K, while the qTPC$_{60}$ tends to fragment into separated C$_{60}$ units at 1200K.

The complete atomization of the structures occurs at the related melting points, as shown in
Figure 3: Representative MD snapshots for the heating ramp simulations (melting process) for: qHPC$_{60}$ at (a) 0K, (b) 1000K, (c) 1600K, and (d) 4000K, and qTPC$_{60}$ at (e) 0K, (f) 800K, (g) 1200K, and (h) 4000K.

Figures 2(d) and 2(h) for qHPC$_{60}$ and qTPC$_{60}$, respectively. Importantly, the different mechanisms observed in the melting processes are strictly related to their topology. qHPC$_{60}$ presents eight covalent bonds connecting the next-neighboring C$_{60}$ units, whereas qTPC$_{60}$ presents only six. The higher number of covalent bonds in qHPC$_{60}$ favors the formation of LACs before the lattice atomization at 1000K (see Figure 2(b)). Conversely, the qTPC$_{60}$ lower number of covalent bonds is responsible for its fragmentation into individual C$_{60}$ molecules at 800K (see Figure 2(f)).

The stress response as a function of the uniaxial applied strain is illustrated in Figure 4. Figures 4(a) and 4(b) show the stress-strain curves for the uniaxial tensile loading along the x-direction (blue) and y-direction (red) for qHPC$_{60}$ and qTPC$_{60}$, respectively. The first noticeable feature is that these structures have an anisotropic mechanical behavior, which is expected because of their structural anisotropy. qHPC$_{60}$ and qTPC$_{60}$ are more resilient to tension along the x-direction than for the y-one. The presence of a ring composed of four carbon atoms linking the C$_{60}$ units makes these structures less resilient to tension along the y-direction.

In Figure 4, we can note that these materials present a well-defined (linear) elastic region when subjected to uniaxial strain. qHPC$_{60}$ and qTPC$_{60}$ undergo an abrupt transition from integrity to a fractured form after a critical strain of 9.6% (11.9%) along the x-direction (y-direction) and 12.2% (11.6%) along the x-direction (y-direction), respectively. The ultimate stress values for qHPC$_{60}$ and qTPC$_{60}$ are: 20.4 GPa (21.7 GPa) for the x-direction (y-direction) and 13.3 GPa (14.6 GPa) for the x-direction (y-direction), respectively. The ultimate stress is defined as the corresponding tensile stress for a critical strain. In our calculations, 1% of strain was used to estimate the following Young’s modulus values for qHPC$_{60}$ and qTPC$_{60}$: 175.9 GPa (218.5 GPa) for the x-direction (y-direction) and 100.7 GPa (133.5 GPa) for the x-direction (y-direction), respectively. As mentioned above, qHPC$_{60}$ tends to be more resilient than qTPC$_{60}$ due to the higher number of covalent bonds connecting the next-neighboring C$_{60}$ units. These values are much lower than other 2D carbon-based structures and can be explained by the high structural stability of the C$_{60}$ units.

Finally, we discuss the fracture patterns of the qHPC$_{60}$ and qTPC$_{60}$ monolayer when subjected
Figure 4: Stress-strain curves for (a) qHPC$_{60}$ and (b) qTPC$_{60}$ as a function of the uniaxial applied strain in the (blue) x-direction and (red) y-direction.

to uniaxial tensile loading. Figures 5(a-c) and 5(d-f) show representative MD snapshots for the strain applied along the x-direction ($\varepsilon_x$) and y-direction ($\varepsilon_y$) for the qHPC$_{60}$ monolayer. Figure 5(a) and 5(d) illustrate the monolayer configurations at $\varepsilon_x = 0$ and $\varepsilon_y = 0$, respectively. As can be inferred from Figure 5(b), qHPC$_{60}$ preserves its topology as the strain increase up to $\varepsilon_x = 11.9\%$. Immediately after this critical strain value, the lattice breaks abruptly with fast and linear crack propagation along the opposite direction of the stretch (see Figure 5(c)).

For the qHPC$_{60}$ stretching along the y-direction, a non-linear fast crack propagation is observed along the opposite direction of the stretch at 9.8% of strain, as shown in Figure 5(e). The total fracture of qHPC$_{60}$ is achieved at 9.9% of strain (see Figure 5(f)). The anisotropic trend for the fracture patterns of qHPC$_{60}$ is due to the different bond arrangements that connect the next-neighboring C$_{60}$ units along the directions of this 2D crystal. For the x-direction, four diagonal bonds connect a central unit to four neighboring units. On the other hand, along the y-direction, there are four parallel bonds linking only two neighboring units with a central one.

Figures 6(a-c) and 6(d-f) show representative MD snapshots for the strain applied along the x-direction ($\varepsilon_x$) and y-direction ($\varepsilon_y$) for the qTPC$_{60}$ monolayer. Figure 6(a) and 6(d) depict the monolayer configurations at $\varepsilon_x = 0$ and $\varepsilon_y = 0$, respectively. We can note that the equilibrated qTPC$_{60}$ monolayer is not planar. It preserves its topology as the strain increase up to $\varepsilon_x = 12.4\%$ (Figure 5(b)) and to $\varepsilon_x = 11.2\%$ (see Figure 5(e)). Immediately after these critical strain values, the lattice breaks linearly with a fast crack propagation along the opposite direction of the stretch for $\varepsilon_x = 12.5\%$ (Figure 5(c)) and $\varepsilon_y = 11.3\%$ (Figure 5(f)). The same abrupt fracture mechanism occurs when the qTPC$_{60}$ is stretched along the x and y direction. Since the central C$_{60}$ unity in qTPC$_{60}$ is connected only with parallel covalent bonds to its next-neighboring units, the fracture pattern is the same regardless of the crystal direction.

4 Conclusions

In summary, We have carried out fully-atomistic reactive (ReaxFF) MD simulations to investigate the thermodynamic stability and stress resilience of qHPC$_{60}$ and qTPC$_{60}$, which were synthesized
very recently [16]. These structures are 2D carbon-based materials composed of closely packed quasi-hexagonal and quasi-tetragonal crystalline phases of C_{60} molecules.

Their melting processes were investigated by employing heating ramp simulations, with temperatures varying from 300K to 10000K during one ns. qHPC_{60} and qTPC_{60} maintain their structural integrity up to 3500K. After this critical value, the thermal vibrations impose substantial changes in their morphologies, and the melting process occurs. We obtained similar melting points of 3898K and 3965K for qHPC_{60} and qTPC_{60}, respectively. The melting process of these structures occurs differently. For the qHPC_{60}, the C_{60} units are fragmented into several linear atomic chains (LACs) at 1600K. The qTPC_{60} structure, in turn, tends to fragment into separated C_{60} units at 1200K.

For the stress response as a function of the uniaxial applied strain, the first noticeable feature is that qHPC_{60} and qTPC_{60} have an anisotropic mechanical behavior. They are more resilient to tension along the x-direction than along the y-one. The presence of a ring composed of four carbon atoms linking the C_{60} units makes them less resilient to tension along the y-direction. Moreover, these materials present a well-defined (linear) elastic region when subjected to uniaxial tensile loading.

qHPC_{60} and qTPC_{60} undergo an abrupt structural transition to a fractured form after a critical strain. qHPC_{60} monolayer breaks abruptly with fast and linear crack propagation when stretched along the x-direction. Conversely, non-linear rapid crack propagation was observed by stretching qHPC_{60} along the y-direction. A similar abrupt fracture mechanism occurs when the qTPC_{60} is stretched along the x and y directions. Since a central C_{60} unity in qTPC_{60} is connected only with parallel covalent bonds to its next-neighboring units, the fracture pattern is the same regardless of

Figure 5: Representative MD snapshots for the strain applied along the (a-c) x-direction (\(\epsilon_x\)) and (d-f) y-direction (\(\epsilon_y\)) for the qHPC_{60} monolayer.
The following Young’s modulus values for qHPC$_{60}$ and qTPC$_{60}$ were estimated: 175.9 GPa (218.5 GPa) for x-direction (y-direction) and 100.7 GPa (133.5 GPa) for x-direction (y-direction), respectively. qHPC$_{60}$ tends to be more resilient than qTPC$_{60}$ due to the higher number of covalent bonds connecting the next-neighboring C$_{60}$ units.

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