Supporting Information

Strain Hardening in Graphene Foams under Shear

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1. The parameters of main force field in CGMD

The main force-field parameters of GrFs with various graphene layers from 1-10 are listed in Table S1 where the parameters of 3, 5, 6, 7, 9, 10 layers are further fitted based on the data of 1, 2, 4, 8 layers provided by Cranford and Buehler\(^1\).

|                  | 1-layer | 2-layer | 3-layer | 4-layer | 5-layer | 6-layer | 7-layer | 8-layer | 9-layer | 10-layer |
|------------------|---------|---------|---------|---------|---------|---------|---------|---------|---------|----------|
| mass (kcal/mol)  | 2852.5  | 5705    | 8557.5  | 11410   | 14262.5 | 17115   | 19967.5 | 22820   | 25672.5 | 28525    |
| \(k_T\) (kcal mol\(^{-1}\) Å\(^{-2}\)) |          |         |         |         |         |         |         |         |         |          |
| \(r_0 = 25\) Å  | 470     | 930     | 1396    | 1860    | 2323    | 2787    | 3253    | 3720    | 4190    | 4663     |
| \(k_B\) (kcal/mol) |          |         |         |         |         |         |         |         |         |          |
| \(\theta_0 = 90^\circ\) | 16870   | 33740   | 50610   | 67480   | 84350   | 101220  | 118090  | 134960  | 151829  | 168698   |
| \(k_B\) (kcal/mol) |          |         |         |         |         |         |         |         |         |          |
| \(\theta_0 = 180^\circ\) | 144.9   | 8970    | 28782   | 82731   | 185601  | 351166  | 595220  | 933087  | 1379947 | 1951198  |
| \(\sigma\) (Å)   |          |         |         |         |         |         |         |         |         |          |
| \(\varepsilon = 473\) kcal/mol | 2.98    | 5.96    | 8.78    | 11.92   | 15.20   | 18.35   | 21.27   | 23.84   | 25.89   | 27.30    |

Table S1. The parameters of main force field in CGMD
2. Local (position-dependent) state of stress

On the micro/mesoscale, the virial stress can be considered as a mechanical stress measure, even in the case of a very inhomogeneous phenomena. According to a generalization of the virial theorem, the average virial stress at a volume $\Omega$ around particle $i$ at position $\mathbf{r}_i$ can be expressed as follows

$$\sigma^i = \frac{1}{\Omega} \left( -m \frac{d\mathbf{u}_i}{dt} \otimes \frac{d\mathbf{u}_i}{dt} + \frac{1}{2} \sum_{j \neq i} \mathbf{r}_{ij} \otimes \mathbf{f}_{ij} \right)$$

where $m$ is the mass of particle in the numerical sample, $\mathbf{u}_i$ is the relative displacement of $i$ for the reference position. Hence, the material time derivative of $\mathbf{u}_i$ is the thermal excitation velocity of the particle. The interparticle force $\mathbf{f}_{ij}$ applied on particle $i$ by particle $j$ is

$$\mathbf{f}_{ij} = \frac{\partial \Phi_{ij}}{\partial \mathbf{r}_{ij}} \frac{\mathbf{r}_{ij}}{||\mathbf{r}_{ij}||} \text{ with } \mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$$

where $\Phi_{ij}$ is the total energy of the coarse-grain ensemble, including the bead-spring and rotational-spring and pairwise interatomic potentials, as described previously.

3. Total energy curve of 5-layer GrF during the equilibrium process

Fig. S1 shows the total energy curves of equilibrium process during the two-step preparation, including the realization of energy minimization for initial 5-layer GrF with 100 graphene flakes placed randomly (see Fig. S1a) and for 5-layer GrF after building inter-sheet crosslinks with crosslink density of 0.47 (see Fig. S1b).
Figure S1. Total energy curves during the equilibrium process (a) of initial 5-layer GrF with 100 graphene flakes placed randomly and (b) of 5-layer GrF after building inter-sheet crosslinks with crosslink density of 0.47.

4. The shear stress evolution of GrFs with various graphene layers

Fig. S2 shows the shear stress evolution of GrFs with various graphene layers, where the extent of stress concentration increases with increasing shear strain until reaches the maximum strength, and fracture surface appears eventually.
5. The non-localized fracture of GrFs with various graphene layers

The coefficient of variation $C_v$ of GrFs with various graphene layers from 1 to 10 is much similar as shown in Fig. S3, which decrease rapidly during the yielding stage and get close to zero eventually.

6. The effect of the number of graphene layers

Fig.S4 shows the mechanical responses of GrFs with various graphene layers from 1 to 10. Fig. S4a shows stress-strain relationships indicating that the strain hardening is universal in
GrFs with various graphene layers, and the shear modulus $G$ and the number of graphene layers $n$ satisfy a power scaling law $G \sim n^{1.95}$ as shown in Fig. S4b. Seen from Fig. S4c and Fig. S4d, the more graphene layers, the more broken bonds across the shear loading and the earlier the initial bond-breakings.

Figure S4. The mechanical responses of GrFs with various graphene layers from 1 to 10. (a) The stress-strain relationships. (b) The power scaling law of shear modulus $G$ with the number of graphene layers $n$. (c) The curves of the number of broken bonds. (d) The shear strain at initial bond-breakings.

7. The effect of crosslink density

Fig.S5 shows the mechanical responses of GrFs with various crosslink densities from 0.00 to the saturated value 1.00. Fig. S5a shows stress-strain relationships indicating that the strain
hardening is universal in GrFs with various crosslink densities, and a linear correlation of the shear modulus $G$ with crosslink density is shown in Fig. S5b. Seen from Fig. S5c and Fig. S5d, the more crosslink densities, the more broken bonds across the shear loading and the earlier the initial bond-breakings.

Figure S5. The mechanical responses of GrFs with various crosslink densities $\rho$. (a) The stress-strain relationships. (b) The change rule of the shear modulus $G$ with $\rho$. (c) The curves of the number of broken bonds. (d) The shear strain at initial bond-breakings.

8. The effect of temperature

Fig. S6 shows shear stress-strain relationships of GrFs at various ambient temperature. The curves are much consistent except the slight difference of peak values of shear strength,
indicating that the strain-hardening regime in GrFs is insensitive to temperature.

Figure S6. The stress-strain relationships of 5-layer GrF at various temperature.

References

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