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C4T

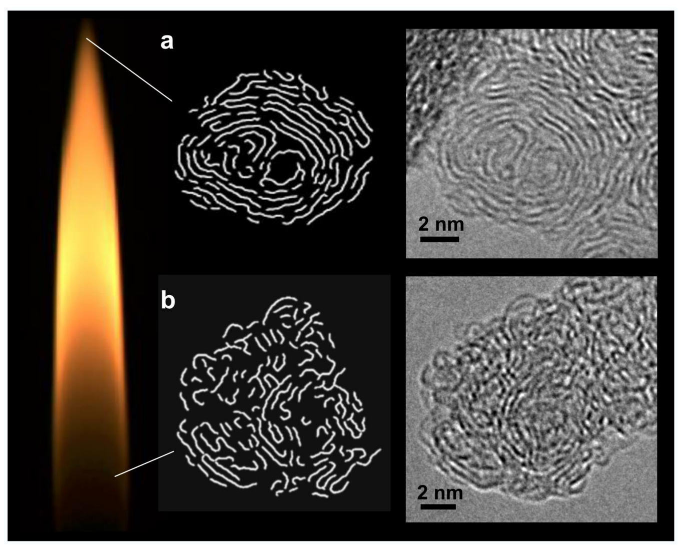
Degree of crosslinking in combustion carbons

INTRODUCTION

Soot particles are formed during incomplete hydrocarbon combustion and have adverse effects on human health and the environment.

- Electron microscopy has revealed soot particles are constituted of aromatic layers, interpreted as the stacking of large polycyclic aromatic hydrocarbons (PAHs).
- MD studies have shown that the binding energy between medium-sized PAHs are not strong enough to stabilize the dimer or trimer from evaporation at high temperatures.
- Nanoindentation experiments show that the hardness of mature soot and carbon black are similar to a hard crosslinked carbon such as charcoal.

These considerations suggest that mature soot and carbon blacks are carbonised and crosslinked and aliphatic chains and bridge formation between aromatic parts play an important role in soot maturation.

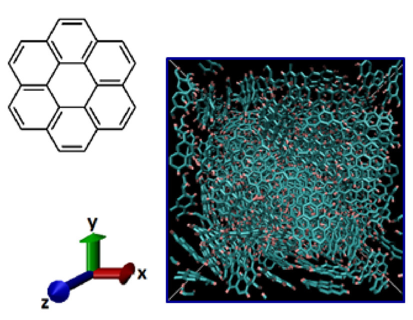


A reactive molecular dynamics (MD) study of mechanical properties of crosslinked PAHs has been made to estimate the degree of crosslinking in combustion carbons

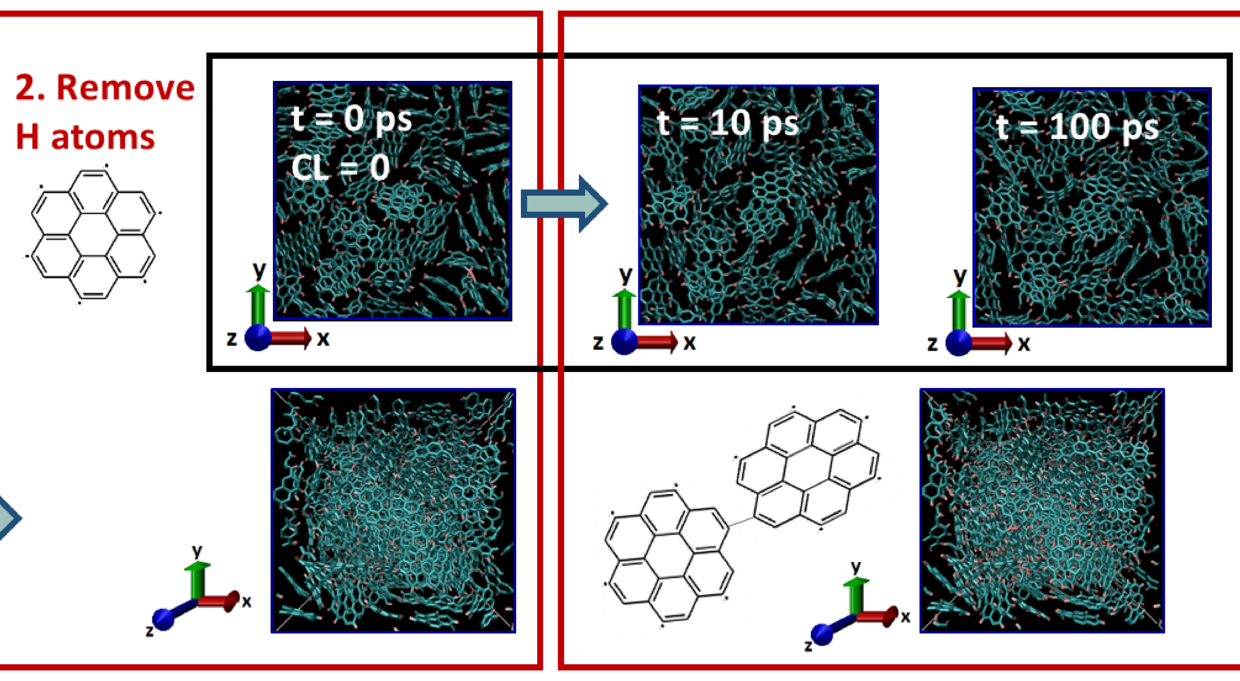
METHODS

1. Packing molecules

PAHs are randomly located in a cubical box :
d=1.5 g/cm^3
periodic conditions



2. Remove H atoms



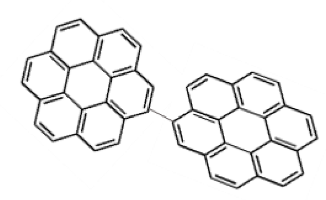
3. Crosslink MD

A reactive force field simulation Is run and halted at different times to provide varying degrees of crosslinking.

Simulation set up:

- *NVT ensemble*
- *Berendsen thermostat*
- *T = 1000 K*
- *timestep = 0.25 fs*
- *simulation time = 100 ps*

4. Add H atoms

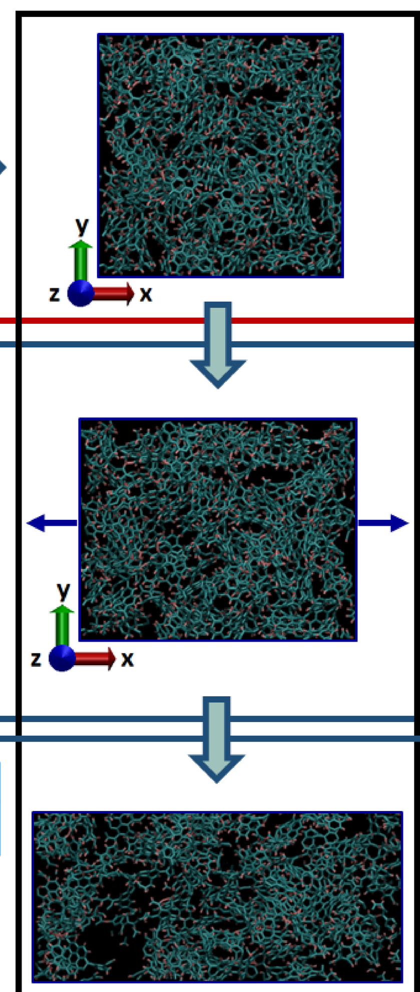


CROSSLINKING PROCEDURE TO BUILD PAH BOXES WITH VARYING DEGREE OF CROSSLINKING

5. Reactive MD simulation of uniaxial tensile test along x direction

Simulation set up:

- *NPT ensemble (Nose-Hoover chain thermostat and barostat)*
- *T = 300 K*
- *P = 1 atm fixed on y and z boundaries*
- *timestep = 1 fs and strain rate = 10^{10} s^{-1}*

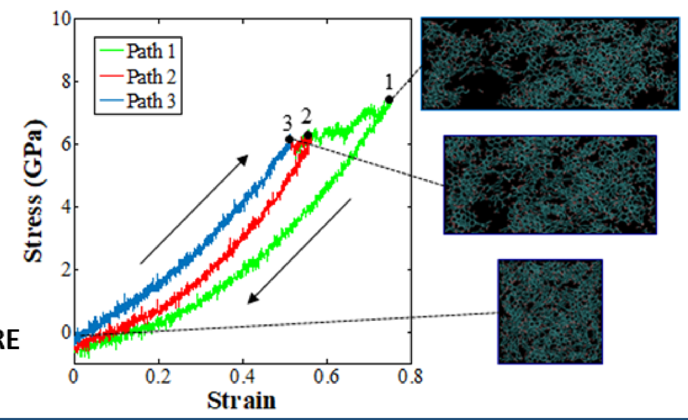


(failure point)

UNIAXIAL TENSILE TEST

6. yield stress (σ_f) identification

LOAD-UNLOAD PROCEDURE



7. Hardness (H) values calculation and comparison.

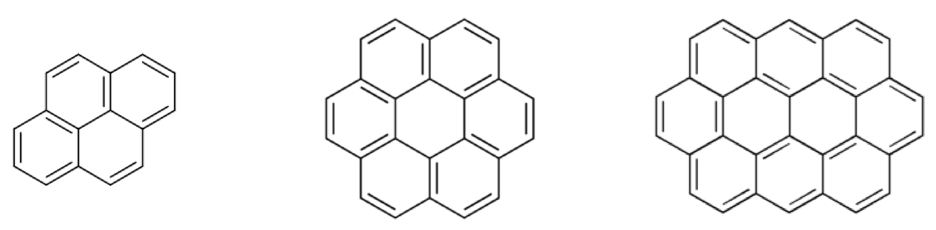
$$H = K\sigma_f \ [4]$$

K has been calibrated with diamond and HOPG cases

COMPARISON WITH EXPERIMENTAL VALUES: NANOINDENTATION EXPERIMENTS ON SOOT (Ref. [3])

The **MD simulations** were carried out using **LAMMPS** [1].

STARTING MONOMERS



FORCE FIELD: an updated version of the adaptive intermolecular reactive empirical bond order, know as AIREBO-M [2].

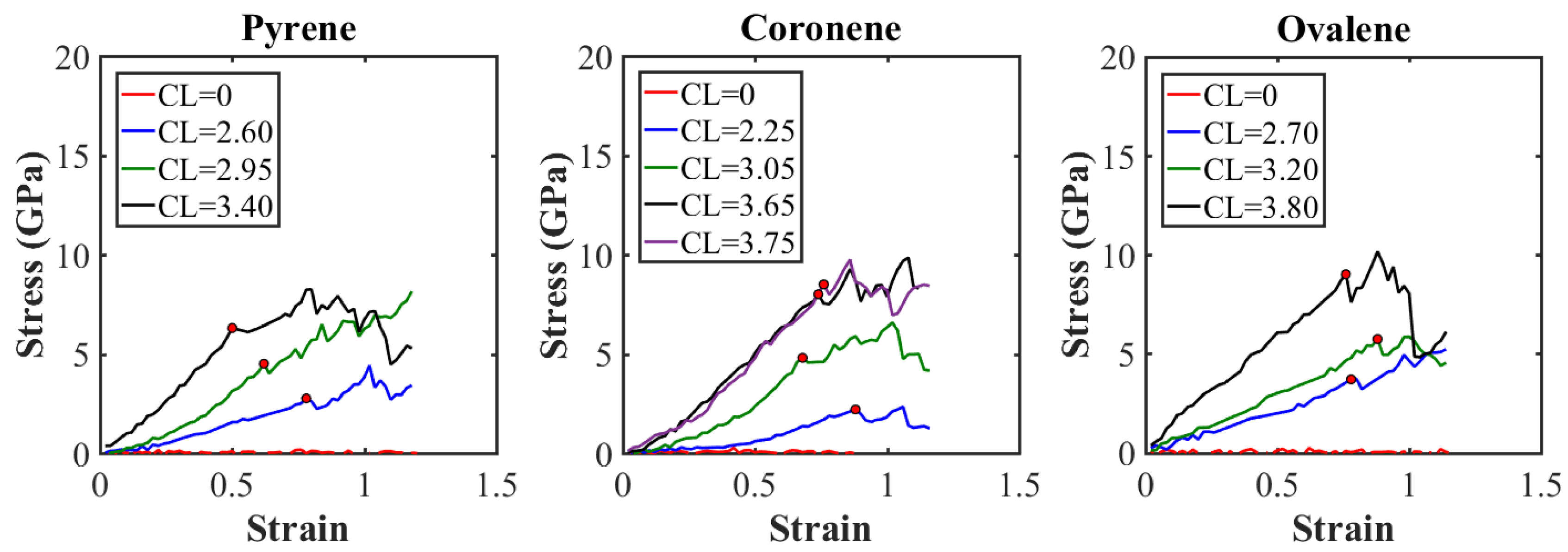
RESULTS

CROSSLINKING PROCEDURE

The degree of crosslinking is defined as:

$$CL = \frac{2 \cdot \text{number of crosslinks}}{\text{number of molecules}}$$

Stress-strain uniaxial tensile curves for pyrene, coronene and ovalene at varying degree of crosslinking (CL). Red circles represent the yield point in each system.



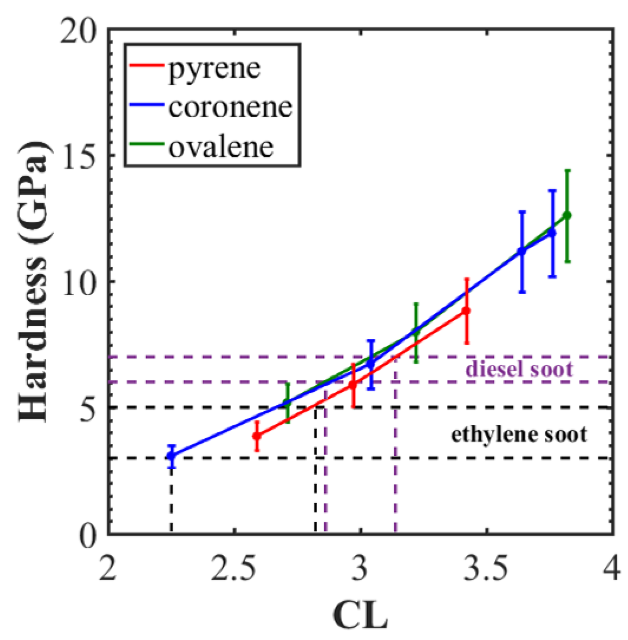
UNIAXIAL TENSILE TEST

yield stress (σ_f) and hardness (H):

$$H = K\sigma_f$$

$$K = \frac{(K_{HOPG} + K_{diamond})}{2} = 1.4$$

Material	σ_f (GPa) MD results (this work)	H (GPa) nanoindentation experiments	Ref.	K
HOPG	1.5	2.4	[5]	1.6
Diamond	83	100	[5]	1.2



H values vs CL using K=1.4 (with error bars showing K=1.2-1.6). H values taken from Ref. [3] for diesel and ethylene soot are also shown for comparison.

- The crosslinking conversion enhances the mechanical properties of the material tested.
- There is a weak dependence on the extension of the aromatic molecule used as monomer.

COMPARISON WITH EXPERIMENTAL VALUES

$$H_{\text{ethylene soot}} = 3 - 5 \text{ GPa } [3]$$

$$H_{\text{diesel soot}} = 6 - 7 \text{ GPa } [3]$$

$$\mathbf{CL \neq 0}$$

$$\mathbf{CL_{ethylene\ soot} = 2.25 - 2.75}$$

$$\mathbf{CL_{diesel\ soot} \sim 3}$$

CONCLUSIONS

- The results show that soot must contain crosslinks between its constituent PAH molecules to have a comparable hardness value found experimentally.
- The results also give information on the possible degree of crosslinking in soot particles. Ethylene soot and diesel soot are expected to have crosslinked densities between 2.25–2.75 and ~3, respectively.

REFERENCES

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