DEGREE OF CROSSLINKING IN COMBUSTION CARBONS

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Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) are essential components of carbonaceous nanoparticles formed in combustion processes. These particles - also known as soot - present a pressing problem to human health and the climate, but can also produce many novel carbon materials used as pigments, reinforcing rubbers and battery anodes. The transition from the gas phase to the condensed phase in combustion processes is poorly understood[1]. Looking at the hardness values of mature soot (3-7 GPa)[2], values closer to a hard crosslinked carbon such as charcoal are found. These results indicate that mature soot particles are carbonised and crosslinked and are not van der Waals solids. Therefore, understanding their degree of crosslinking is important for determining which mechanisms and precursors are involved in their inception and growth. In this work, we performed molecular dynamics (MD) simulations of nanoindentation on combustion-generated nanoparticles aimed to investigate the effects of the particle structure on its mechanical properties.

Materials and Methods

The indentation MD model used in this study is reported in **Figure 1**. The model soot particles are composed by an 'amorphous' core of crosslinked coronene molecules and an outer shell of crosslinked circumanthracene molecules disposed in layers. The degree of crosslinking (CL) was defined as the average number of crosslinks contained in each molecule in the particle. More than fifty different particles were tested to understand the effect of different structural parameters – particle and core radius ($R_{particle}$), shell thickness (d_{shell}) and degree of crosslinking in the core and in the shell (CL_{core} and CL_{shell}) – on the simulated hardness (H). The considered parameter ranges

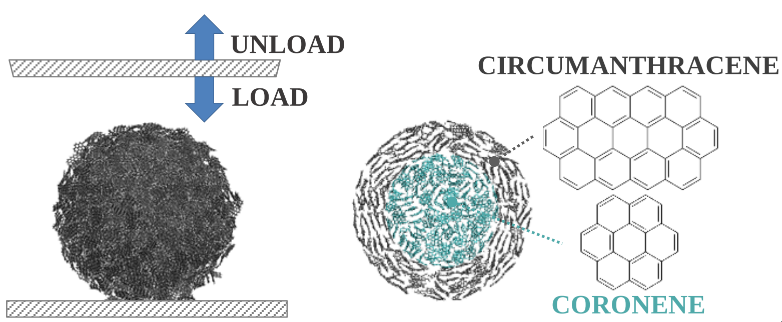

Figure 2. Indentation MD model and model soot particle

Parameter	min	max	units
CL_{core}	0.0	4.0	-
CL_{shell}	0.0	3.0	-
R_{core}	2.25	4.5	nm
d_{shell}	1.0	2.0	nm
$R_{particle}$	3.5	5.5	nm
$d_{shell}/R_{particle}$	0.0	0.5	-

Table 1. Structural parameters of the investigated model soot particles.

are summarized in **Table 1**. A virtual wall was placed at the bottom of the particle and the indentation simulations were performed with a rigid planar indenter that moves down up to a distance of 60% of the particle diameter at a speed of 25 m/s. The potential used is the AIREBO-M potential[3], which has been widely used to investigate the mechanical properties of carbon-based nanomaterials. All the MD simulations were performed using the software LAMMPS.

Results and Discussion

From the load-displacement curves, the hardness (H) can be determined and the following main conclusions can be made:

- For a particle without the shell (young soot), H is very low (order of MPa) when CL is lower than 2 and then it starts to increase linearly to reach a value around 8 GPa at CL=3.5. The results don't change changing the particle size (**Figure 2a**).
- Introducing a shell (mature soot), H is a function of the CL in the core and in the shell and the core/shell ratio (**Figure 2b**). Knowing the core/shell ratio and the hardness of the particle, it is possible to estimate a range of CL in its core and its shell.

The results show that mature soot particles are expected to present crosslinks between their aromatic constituents to have a comparable value of the hardness found experimentally (3-7 GPa)[2]. Moreover, the transition from the liquid-like behaviour that young particles show at flame temperature to the solid state (mature soot) can be explained as an increase of its CL.

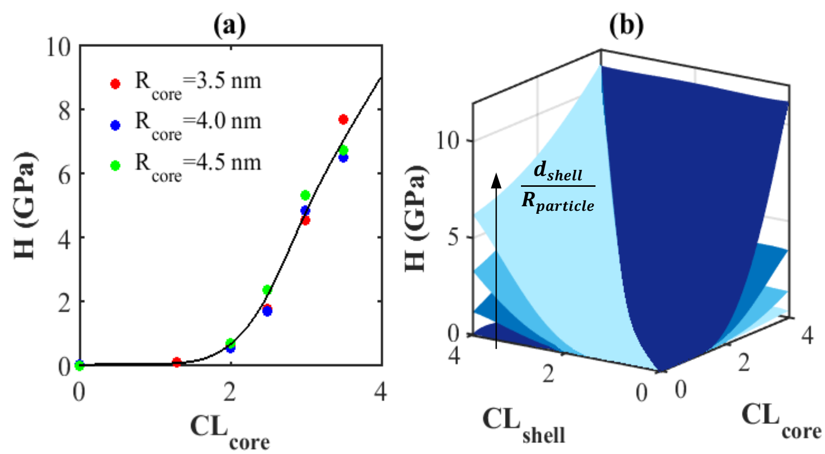

Figure 3. (a) H as a function of CL for particles without shell and with different sizes; (b) Surface plot for H as a function of CL in the core and in the shell at different core/shell ratio.

Conclusions

These results reveal the importance of crosslinking reactions during soot formation and maturation that give rise to a structure in which the majority of aromatics are aliphatically-linked in a 3D network.

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