Approach for Estimating Elastic Behavior of Soot Aggregates with Ultrasmall-angle X-ray Scattering

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Introduction

Soot typically comes as fractal aggregates of primary particles, which can be built up from subunits and elementary units. Depending on the surface properties of primary particles and aggregates, bigger soot clusters or agglomerates can be formed from the aggregates as well. Soot is thus rich in structure that can be probed with ultrasmall-angle x-ray scattering (USAXS). To suppress the scattering from the agglomerates and aggregates and thus concentrate on the scattering of the primary particles, we introduced the pellet technique. In this report, we describe how the USAXS of soot pellets as function of pressure can be used to define an elastic constant for the soot.

Methods and Materials

Soot was produced at the diesel engine test facility at the University of Utah from three diesel fuels in a two-stroke diesel test engine operated under idle and load conditions. An oxygenated diesel/diethylene carbonate mixture was used as the fuel. The soot was collected on quartz filters, then separated from the filters for further analysis. Soot pellets about 1-mm thick and 6 mm in diameter were pressed at a pressure up to 8.5 GPa. Soot distributed on scotch tape was assigned a very low pressure, and soot dispersed in acetone was assigned no pressure at all. USAXS was carried out by using synchrotron radiation at UNI-CAT beamline 33-ID at the APS [1]. At this beamline, a Bonse-Hart setup allows one to record USAXS scattering curves (SCs) by using a photodiode detector with an angular resolution of 0.0001 $Å^{-1}$ at a q-range of 0.0001 to 1.0 $Å^{-1}$. The SCs were desmeared and background-corrected with the beamline-specific software. The data acquisition time for an SC with 150 equidistant data points over the q-range was typically 15 minutes per sample. All USAXS data were fully corrected for all instrumental effects. The x-ray energy was 10,000 eV.

Results and Discussion

SCs of soot powder, pellets, and soot powder dissolved in acetone are shown in the left image of Fig. 1. The upper SC with open symbols is from the soot powder and shows a hump at q = 0.02 $Å^{-1}$ — this is the signature of the soot aggregates.

Upon being pressed, aggregates become more dense and finally lose their characteristic structure. The SC of a slightly pressed pellet is shown in the uppermost curve with filled symbols. There, a shift of the hump toward a larger q is observed. Upon further pressure, the hump moves even further to large q-vectors and finally vanishes, as shown in the other SC with filled symbols. Here, the hump finally forms a Guinier intensity bending region, with an intensity plateau toward the lower

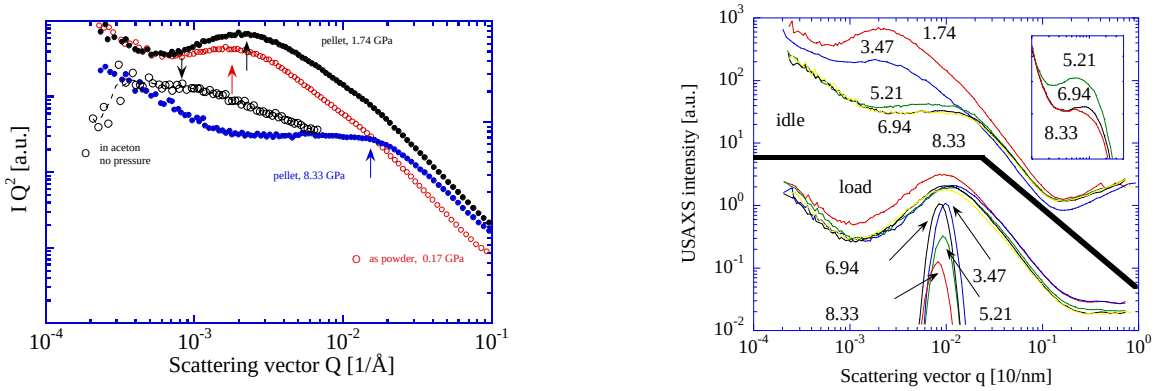

FIG. 1. Image on the left shows SCs of soot powder, pellets, and soot in acetone. Image on the right shows SCs of soot for various pellet pressures under idle and load conditions. Insets are magnifications; numbers are pellet pressures in GPa.

q-vectors and a power law regime toward a larger q. After dispersion of the soot powder in acetone and ultrasonication, agglomeration should be destroyed. This would basically simulate the state with no pressure on the aggregates at all. Indeed, in the lower SC with open symbols, a slight hump can be seen at the smaller q-range side at about q = 0.0008 $Å^{-1}$. The position of this hump on the q-axis indicates directly the size of the aggregates due to the reciprocal relationship between scattering vector and real-space metric. The image on the right in Fig. 1 shows the SC of a soot sample under idle (top) and load (bottom) conditions. The insets show magnifications of the important q-ranges for better discrimination. Numbers indicate the applied pressure in GPa for pellet production. The soot under load conditions (bottom) shows less variation of the SC with increasing pressure and thus seems to be not as compressible as the soot under idle conditions. We carried out other extensive analyses of the soot idle/load issue [2-4] and found there could be significant differences, which in part may be caused by significant differences in the presence of volatiles, residual oil, and fuel in the soot. The idle soot of oxygenated diesel fuel showed particularly more volatiles, for instance. For idle soot, we found that the variation in the intensity hump attributed to the aggregate structure was stronger than it was for the load soot. The idle soot seemed more elastic. We thus defined an elastic constant for soot, based on the pressure/elongation relationship of the aggregate structure.

From the position of the maximum on the q-axis, the aggregate size x was determined by using $x = \pi/q$. The sizes ranged from 470 to 34 nm for the idle soot aggregates and 73 to 33 nm for the load aggregates. The larger size of both sets is considered x_o, and the elasticity constant is then $\Delta P/\Delta x = P/x - x_o$. This quantity is plotted versus the pellet pressure in Fig. 2. Both soot samples

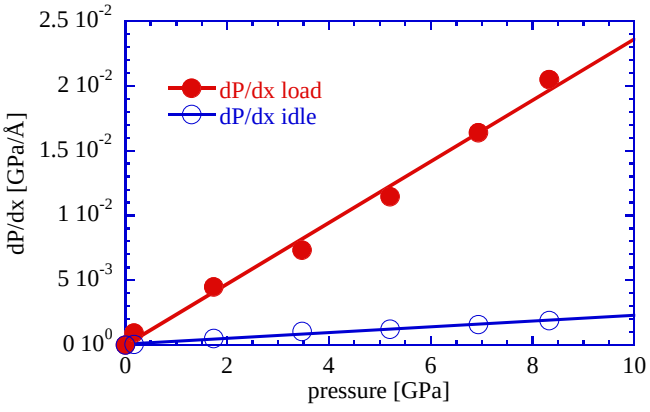

FIG. 2. Evolution of the elasticity constant of idle and load soot from oxygenated diesel fuel with pellet pressure.

show a linear variation of the so-determined elasticity "constant." However, it is obvious that the load soot shows less variation and appears stiffer than the idle soot.

Creative handling of samples, combined with a state-of-the-art analytical technique like USAXS, can help researchers derive additional information about the samples, such as their elastic properties. The elastic properties of nanoparticles are frequently studied with scanning probe techniques (e.g., by applying tip force to sot particles) or carbon nanotubes. The experiment performed here basically uses a similar approach. Carbon black, for instance, is basically a soot material that is used as a filler for many purposes, including its use as a filler in tires for automotive applications. To reduce its volume for shipping purposes, it is sometimes pressed in pellets, and after shipment, it is crunched again and used as filler. The sustainability of its elastic properties might play a role in helping it serve its purpose as filler material. We can speculate about the use of elastic properties of soot in diesel engines. The wear and tear on engine surfaces might play a role, for instance.

Acknowledgments

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