

# Micrometer-scale Experimental Characterization of the Lower Huron Shale in the Central Appalachian Basin

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## Introduction

The mechanical properties of shale play an important role in hydraulic fracturing design. Although the popular nanoindentation method can be performed to evaluate some mechanical characteristics of organic matter, it is still difficult to fully characterize mechanical properties of organic components of shale due to their small scale which is usually on the order of micrometers or even nanometers. As a novel material characterization tool, Atomic Force Microscopy (AFM) has shown great potential to characterize surface properties and pore structures at micrometer- and nanometer-scale and has been applied to investigate the elastic properties of organic components in shale by multiple researchers.

Raman and FTIR can detect chemical bands by utilizing molecular vibration information. Because Raman and FTIR measurements are non-destructive, high sensitivity, and short in duration, they have been used extensively to study maturation processes of organic components in coal and shale samples. To some extent, these two methods can be considered as complementary to each other, and more comprehensive understanding about maturation processes of organic components can be achieved by combining these two methods.

In this work, mechanical properties and chemical characteristics of four shale samples with different thermal maturities were investigated. Generally, this study had two objectives: (1) Characterize the mechanical properties of shale samples with different maturity levels through the novel AFM method, and (2) Explore the underlying cause for the change in elastic properties of shale samples from a chemical perspective through the complementary Raman and FTIR methods.

## Methodology

### Samples:

	Sample 1	Sample 2	Sample 3	Sample 4
Depth (feet)	5581-5582	6132-6133	5498-5499	5545-5546
Ro (%)	0.95	0.98	1.18	1.28

Ro (%): Tested vitrinite reflectance value

### Raman Measurement:

Raman experiments were conducted through a HORIBA LabRAM HR Confocal Raman Microscope at room temperature. Excitation wavelength was 532nm and signal collecting time is 20 seconds. The range of wavenumber in measurement extends from 400 cm<sup>-1</sup> to 4000 cm<sup>-1</sup>.

### FTIR Measurement:

FTIR measurements were conducted through a Bruker ALPHA FTIR spectrometer. The scan range for the FTIR test is 400-4000 cm<sup>-1</sup> at the resolution of 2 cm<sup>-1</sup>. Each sample was tested twice and no difference was found between the repeated measurements.

### AFM measurement:

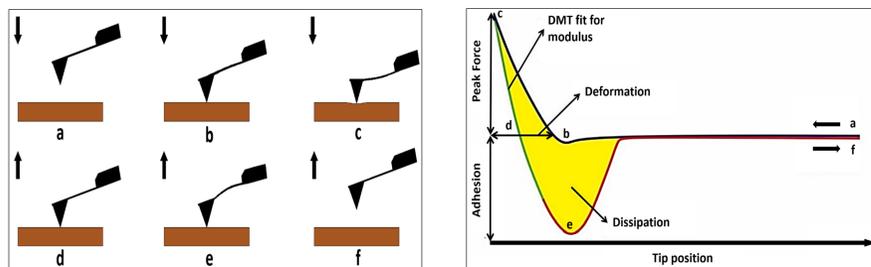


Fig. 1. Schematic illustration of scanning process and AFM Force-distance curve

- tip is far away from sample surface and no force acting on the tip.
- tip starts approaching sample surface and cantilever starts bending due to attraction force from sample surface.
- tip stays on sample surface and force reaches the set constant peak force.
- deformation of the cantilever equals to zero and adhesion force is applied.
- the maximum adhesion force between tip and sample surface is given.
- separate process completes and the force acting on tip becomes zero again.

## Results

### Raman Characteristics:

Fig.2 indicates there are two peaks for each sample at around 1340 cm<sup>-1</sup> and 1590 cm<sup>-1</sup>. Normally, they are known as D band and G band. D band represents disorder degree in atoms and is caused by the defect of carbon lattice, G band represents graphite and arise from the in-plane stretching vibration of carbon atoms in sp<sup>2</sup> carbon structures.

## Results (continued)

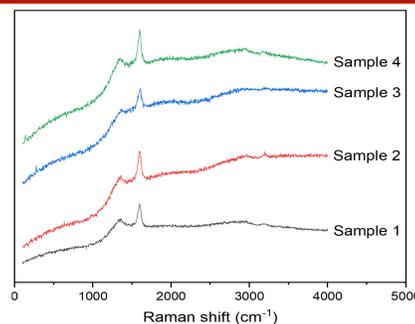


Fig. 2. Raman curves of four shale samples

Due to the overlap of chemical bands, some important information about chemical structure is obscured. As a result, the deconvolution (curve-fitting analysis) process is imperative for further investigation of chemical characteristics of these shale samples. The curve-fitting result for sample 4 is demonstrated in Fig. 3 as an example.

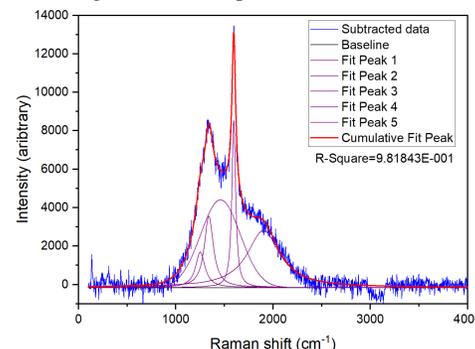


Fig. 3. Curve-fitting result of Raman spectrum (take sample 4 as an example)

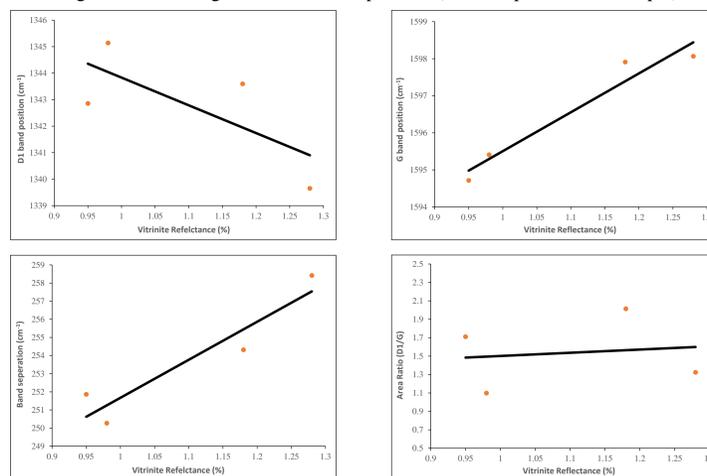


Fig. 4. Relationship between Raman parameters and vitrinite reflectance value: (a) D1 band position; (b) G band position; (c) band separation; (d) area ratio (D1/G)

### FTIR Characteristics:

FTIR curves of scanned samples can be seen in Fig.5. There is no big difference in band positions among these curves, which means similarity in the chemical characteristic and functional bands composition of these samples.

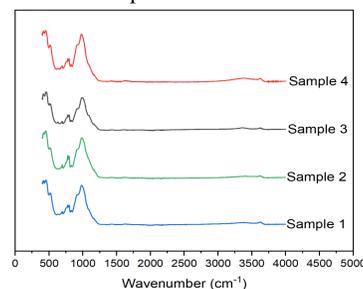


Fig. 5. FTIR curves of four shale samples

## Results (Continued)

Due to the overlap among chemical bands, three curve-fitting regions :700-850 cm<sup>-1</sup>, 850-1300 cm<sup>-1</sup>, 3000-3600 cm<sup>-1</sup> were chosen to further investigate function groups in the aromatic, oxygen-containing and hydroxyl region.

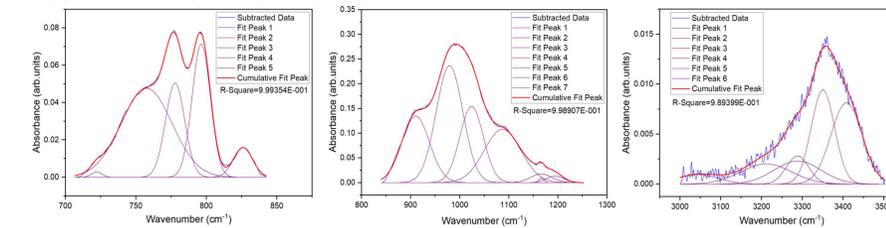


Fig. 6. Curve-fitting results of selected FTIR spectrum (take sample 3 as an example)

### AFM Characteristics:

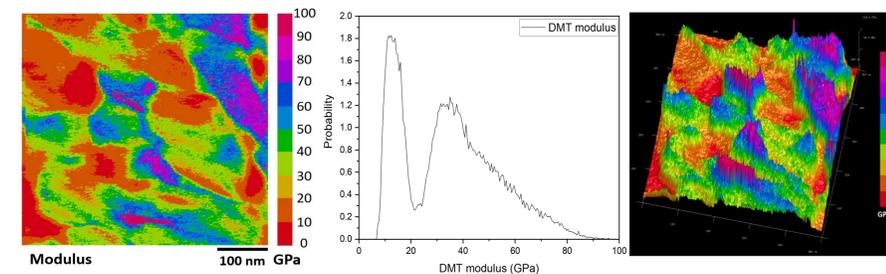


Fig. 7. Modulus map and distribution of sample 4 (Modulus value was cur-off at 100 GPa)

## Discussion

The following indexes calculated from FTIR spectrum were selected to characterize: (1) aromaticity; (2) condensation of aromatic rings; (3) length of aliphatic chain. Calculation methods are listed in Table 1, calculated results and mode modulus value from AFM are listed in Table 2.

Table 1. Calculation methods for parameters derived from FTIR spectrum

Indexes	Calculation method
I <sub>1</sub> (Aromaticity)	A <sub>3000-3100</sub> /A <sub>2800-3000</sub>
I <sub>2</sub> (Aromaticity)	A <sub>700-900</sub> /A <sub>2800-3000</sub>
DOC (Degree of condensation)	A <sub>700-900</sub> /A <sub>1600-1610</sub>
CH <sub>2</sub> /CH <sub>3</sub> (Aliphatic chain length)	A <sub>2900-2940</sub> /A <sub>2940-3000</sub>

Table 2. Indexes calculated from FTIR spectrum and mode modulus value from AFM

Sample	Sample 1	Sample 2	Sample 3	Sample 4
Ro (%)	0.95	0.98	1.18	1.28
I <sub>1</sub>	0.57	0.62	0.52	0.78
I <sub>2</sub>	9.06	15.92	5.44	19.42
DOC	215.25	260.67	152.45	297.71
CH <sub>2</sub> /CH <sub>3</sub>	0.65	0.63	0.65	0.56
Mode value	13.32	14.82	9.01	15.32

According to curve-fitting results from Raman spectrum, the G band tends to increase and D1 band tends to decrease with increasing maturity level. The shift of the G band and D1 band positions can be regarded as the result of the rise of aromatic groups and the decrease of the disorder degree of organic structures. Similar changes in the variation of chemical structure can also be inferred from parameters calculated using FTIR spectroscopy. With the increase of aromaticity level, the modulus value tends to increase, with the exception of the anomalous result obtained from shale sample 3. However, one observation for sample 3 is that its lowest modulus value corresponding to the lowest I<sub>1</sub>, I<sub>2</sub>, and DOC value, and highest CH<sub>2</sub>/CH<sub>3</sub> value.

## Conclusion

- The AFM PeakForce QNM (Quantitative Nano-Mechanical) tapping mode has potential to determine the distribution of modulus value (heterogeneous property) at micrometer or even nanometer scale.
- The modulus value of scanned samples varies from 8.20-12.94 GPa, and it seems that the "softer" organic matter is surrounded by "stiffer" organic matter.
- Changes in mechanical properties show potential association with changes in chemical structure during maturation process. Specifically, the increase of aromatic groups and the decrease of CH<sub>2</sub>/CH<sub>3</sub> ratio that occur during the maturation process may contribute to the increase of modulus value of organic components.