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Full Length Article

Application of PeakForce tapping mode of atomic force microscope to characterize nanomechanical properties of organic matter of the Bakken Shale

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ABSTRACT

Organic-rich shale, which is a heterogeneous material, has been studied extensively from various perspectives. Among all the components that constitute shale, organic matter is less known in regards to its mechanical properties. Since organic matter is relatively the softer part compared to inorganic minerals, high concentrations of it can have a significant impact on bulk mechanical properties of the rock, which can affect field operations such as hydraulic fracturing. In this study, four shale samples from the Bakken Formation in Williston Basin, North Dakota, were examined by a combination of experimental methods including X-ray diffraction (XRD), Rock-Eval pyrolysis, optical and scanning electron microscopy (SEM) along with atomic force microscope (AFM). PeakForce Quantitative Nano-mechanical Mapping mode in AFM was used particularly, to map the modulus of organic matter in nano-scale. XRD analysis showed that quartz and clays are the main constituent minerals in the shale samples. Geochemical results showed that all samples are extremely organic-rich, and the organic matter is mostly type II, varying from thermally immature to oil generation window. Elastic properties test results demonstrated that surface topographic features including pores, microfractures and grain boundaries would have a negative impact on AFM data, and a data filtering procedure was conducted on AFM data to get rid of wrong values. The elastic modulus of identified organic matter (bitumen and micrinite) was measured in the range of 7–23 GPa with a significant heterogeneity in a single studied organic particle and dependent upon the type of organic particle.

1. Introduction

Shale, as unconventional reservoir rock, have changed the global energy structure since the application of technological advances such as horizontal drilling and hydraulic fracturing, which has made production from such tight rocks possible [1–6]. Organic matter is a major component of unconventional shales, and thus its elastic properties and spatial distribution would play an important role in bulk geomechanical properties of the rock. This becomes very important from various angles including processing and inversion of seismic data to obtain elastic modulus and predicting fracture propagation for stimulation purposes [7–9]. Conventional rock mechanical testing such as uniaxial and triaxial compressive strength tests, along with ultrasonic measurements have been used extensively to evaluate mechanical properties of shale rocks at core plug scale or above [10–13,62]. Since shales are very complex in constituent components and abundant in organic matter, there has been a growing interest to study the mechanical properties of each individual component in shales including both organic matter and inorganic minerals in micro and/or nano-scale [14–20]. Among all these constituent components, organic matter has been studied the least due to several limitations such as: lack of advanced equipment with adequate resolution to isolate organic matter independently from other components, lack of standard procedures for performing these studies, and most importantly, the variations that exist in the organic matter due to its biogenic origin and maturity conditions. Due to all these restrictions, there is not a substantial database of organic matter

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modulus of elasticity that can be used for further analysis, upscaling and modeling purposes.

Despite the limitations, some attempts have been carried out in recent years to examine nanomechanical properties of organic matter within shale rocks. Most of these studies are based on the nanoindentation technique, which involves probing an indenter of known geometry and mechanical properties to the material surface, while simultaneously measuring the force and displacement. In summary, Mba and Prasad (2010) reported Young's modulus of 33 GPa as the upper limit for organic matter and/or clay minerals combined [10]: Alstadt et al. (2015) reported Young's modulus of 5–11 GPa and hardness values of 0.9–1.3 GPa for the organic matter in Green River Shale by analyzing the morphology of load–displacement curves [15]. Young's modulus of 6 GPa was reported for the organic matter in the Woodford Shale by marking the organic matter with etched grooves [21]. Furthermore, some researchers studied the effects of thermal maturity on mechanical properties of organic matter, where both increasing and decreasing values were reported as maturity increased [22–25,63]. In spite of the benefits of nanoindentation, it can only produce discrete points on the surface of the samples, leading to measurements at the micro-scale instead of nano. Moreover, it becomes challenging to relate indentation characteristics to a specific phase because of restrictions in the instrument navigation abilities on the specimen [18,26]. Moreover, most of these studies used indirect methods to find the correct values that correspond to the organic matter modulus by either assuming a possible range based on the existing minerals in the samples or by evaluating the overall characteristics of the load-displacement curves, through data deconvolution. This shows the disadvantages of nanoindentation to relate measured modulus to organic matter properties, such as composition, maturity and biogenic origin.

AFM is a powerful technique in characterizing nano-scale mechanical properties. The PeakForce quantitative nanomechanical mapping (PF-QNM), a relatively new tapping mode (Mark of Bruker Nano Surfaces), can provide the quantitative mechanical map at high resolutions. The calculation of modulus is based on the force-displacement curve. To be more specific, a constant peak force is applied by a very fine tip, which generally has a radius smaller than 100 nm [27,28], and then the deflection of the cantilever is measured. In the next step, the force-displacement curve can be derived during the scan for each pixel in the order of nanometer to calculate the Derjaguin-Muller-Toporov (DMT) modulus [29]. At the same time, parameters such as topography, deformation, adhesion, and dissipation can also be derived from the force-displacement curve. This technique has been used extensively utilized to mechanically characterize polymers, biological and cement materials [30–33]. Considering the advantages of AFM PF-QNM, this technique enables us to study spatial variations of mechanical properties across a surface at nano-scale without any impact from the underlying phase. In this regard, in the geosciences, a few researchers have taken the advantage of this method to examine the mechanical properties of shale components, either organic phase or inorganic minerals. Eliyahu et al. (2015) reported the first application of this technique on shale samples [34]; Emmanuel et al. (2017) examined the effects of thermal maturity on elastic properties of organic matter by AFM PF-QNM on Cretaceous shales and reported an increasing trend of modulus as maturity increased, and documented softening of organic matter in reservoir temperatures [35]. Liu et al. (2017) also studied the effect of maturity on mechanical properties on solid bitumen using the same technique [36]. Yang et al. (2017) integrated AFM PF-QNM with nano-infrared spectroscopy to characterize geochemical and geomechanical properties of organic matter on specific macerals to include biogenic origin and type and remove variability to some extent [37]. Considering the limited published data on organic matter mechanical properties, this study is another attempt to assess mechanical properties of organic matter on the Bakken Shale which is one of the most important unconventional shale plays in the U.S. We combined several analytical methods, including Rock Eval pyrolysis, SEM-EDX and organic petrography to, first, understand type and thermal maturity level of the organic matter of our samples, locate the organic matter particle within the samples, analyze its texture and finally measure its mechanical properties using AFM PF-QNM.

2. Geological setting, samples and methods

2.1. Geological setting and samples

The Bakken Formation (Devonian - Mississippian in age) located in the Williston Basin and is a relatively thin rock unit with three distinct members: upper and lower dark shale members and middle detrital/carbonate member, with the total interval thickness ranging from 70 to 100ft (Smith and Bustin, 1996). The two shale members are extremely organic-rich, with an average total organic carbon (TOC) content of 8 wt%, and a maximum of 30 wt%. Four shale samples from the Bakken Formation taken from different wells with various depths were analyzed in this study. According to the depth of each sample, they were labeled as Sample 1 to Sample 4. Sample 1, Sample 2 and Sample 4 were from the Upper Bakken, while Sample 3 was selected from the Lower Bakken.

2.2. XRD, Rock-Eval, and SEM

First, XRD analysis was conducted to obtain mineral compositions. For this purpose, rocks were crushed into 1-5um in size, and then 1–2 cm^3 per sample were placed in the equipment to obtain mineral assemblages.

In the next step, the Shale Play® method (registered trademark of the Institut Français du Pétrole), which is also known as the multiple heating rate (MHR) method, was used to obtain organic geochemistry parameters of the samples, maturity specifically. For this purpose, the initial temperature in the pyrolysis oven was set at 100 °C, then the temperature was increased up to 200 °C at 25 °C/min and held constant for 3 min (for thermal extraction of lightest hydrocarbon fraction; Sh0 or C1-C15), then increased to 350 °C at 25 °C/min where it stayed isothermal for 3 min (for thermal extraction of the medium/heavy hydrocarbon fraction; Sh1 or C15-C40), and finally to 650 °C at 25 °C/min (for thermal cracking of the NSO or kerogen fraction; Sh2). Romero-Sarmiento et al. (2016) and Carvajal-Ortiz and Gentzis (2018) have explained this method in detail and we direct the readers to them for further information [38,39].

Scanning electron microscope (SEM) was employed in this study to help locate organic matter within the samples and to enable accurate navigation on the surface of the sample for the main part of this study, which is force spectroscopy by AFM. In addition, SEM allowed us to study the morphology and various characteristics of the organic matter [40–42], which is described in the following sections. To make navigation on the samples with the AFM easier for mechanical measurements, a large area was first scanned under the SEM and then organic matter was located within that area. In the next step, the exact location desired for moduli measurement was marked relative to pyrite minerals surrounding the organic matter. Pyrite illuminates under optical microscope that is mounted on the AFM and facilitates finding the exact identified location of organic matter easier [34].