Review of Kerogen’s Geomechanical Properties: Experiments and Molecular Simulation

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ABSTRACT: Measuring the mechanical properties of kerogen, the predominant constituent of organic matter in shale is exceedingly difficult as it constitutes small-scale aggregates interspersed in rocks. Kerogen is characterized by significantly lower stiffness compared to inorganic minerals, thereby the kerogen regions are potential areas for study during, for example, drilling or macroscopic fracture propagation in the course of hydraulic fracturing. For instance, the elastic modulus of kerogen-rich spots is around 10 GPa, while it is about 70 GPa for quartz. Failure of the kerogen nanocantilever beam shows an elastic strain-hardening behavior, indicating a higher energy requirement to propagate a crack. Studies illustrated that the kerogen’s mechanical properties are controlled by maceral composition and are positively correlated to the maturity level. This paper provides a comprehensive review of how the mechanical properties of kerogen are elucidated experimentally and contrast the results with the properties delineated from molecular simulation. In addition, we relate kerogen innate attributes, such as maturity and type, to the physical qualities measured and substantiate why accurate knowledge of the mechanical characteristics is pivotal from a hydraulic fracturing perspective.

1. KEROGEN DEFINITION AND CLASSIFICATION

The word kerogen, a portmanteau of the Greek words for wax (keros: wax) and birth (-gen: birth), was coined by Crum Brown in 1906 to label the organic matter (OM) in oil shale that generates a waxy hydrocarbon upon distillation.1 Originally, the definition was limited to waxy oils up until 1980, when Durand generalized the term to encompass all insoluble sedimentary OM, for example, pure humic acids, algal coals, asphaltic substances, and insoluble organic matter in the soil. The chemical structure of macromolecular OM is subject to change due to degradation and condensation reactions, governed by pressure, temperature, and the presence of oxidizing or reducing atmospheres.2

Both OM’s chemical and physical properties are predominately a function of maturation level and source. Depending on the origin and depositional environment, kerogens are grouped into four main types (see Table 1):

- Type I kerogen: highly aliphatic and immature in nature with hydrogen-to-carbon (H/C) ratios greater than 1.5 and low oxygen to carbon (O/C) fractions. This type of OM is associated with a lacustrine depositional environment. Although bearing a greater oil potential than any other type of OM, it is also suggested that Type I kerogen constitutes only three percent of global petroleum resources;

- Type II kerogen: characterized by many aromatics and greater quantities of aliphatic compounds compared to Type I. Sulfur is consistently associated with this type of OM, either as pyrite or free sulfur. This variety is correlated with a deep marine depositional environment comprised primarily of plankton;

- Type III kerogen: derived from higher plant debris and frequently deposited in shallow marine environments. This kerogen category is considered hydrogen-poor and oxygen-rich OM;

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Table 1. Summary of Kerogen Types and Their Properties

| Kerogen type | Maturity level   | H/C   | O/C   | Density of final configuration, (g/cm³) | Formula                  |
|--------------|------------------|-------|-------|---------------------------------------|--------------------------|
| KIA          | Immature         | 1.53  | 0.052 | 0.994                                 | C12H18O3N3Sx              |
| KIIA         | Immature         | 1.17  | 0.095 | 1.126                                 | C12H18O3N3Sx              |
| KIIIA        | Immature         | 0.87  | 0.116 | 1.195                                 | C12H18O3N3Sx              |
| KIIB         | Top of oil window| 1.12  | 0.06  | 1.103                                 | C12H18O3N3Sx              |
| KIIC         | Middle/end of oil window | 0.91  | 0.054 | 1.168                                 | C12H18O3N3Sx              |
| KIID         | Overmature       | 0.58  | 0.051 | 1.240                                 | C12H18O3N3Sx              |

Figure 1. Indentation sequence during testing.

- Type IV kerogen: distinctively hydrogen-poor and oxygen-rich. This OM is frequently combined with Type III.

Kerogen types, evolution, and statistical chemical models have received particular attention between 1970 and 1990 to understand hydrocarbon formation potential. Robust isolation procedures were established to perform physicochemical analyses, and kinetic frameworks were developed to describe the hydrous pyrolysis of kerogen into petroleum as a function of temperature and pressure.

Carbon quantification was not possible with infrared (IR) and ultraviolet (UV) technologies until the development of solid-state 13C NMR spectroscopy enabled quantifying contributions of aromatic and aliphatic groups. Recently, Donadelli et al. presented a study exploiting X-ray photoelectron spectroscopy (XPS) to nondestructively investigate kerogen type and maturity in source rock without necessitating isolation. The analysis characterized the chemical structure of kerogen, specifically the carbon species. The newly proposed parameters in the analysis were: %Cox/OCxps, defined as the ratio of carbon to oxygen species compared to total organic carbon, and the relative content of aromatic carbon, ArP. Their work substantiated a correlation between kerogen origin and %Cox/OCxps, thus rendering recognition of changes in kerogen type possible. Furthermore, they were able to relate conventional maturity indicators like vitrinite reflectance to aromaticity enabling direct exploitation of XPS to delineate kerogen maturity.

2. GEOMECHANICAL PARAMETERS AND EXPERIMENTAL TOOLS

With kerogen generally yielding weaker geomechanical properties compared to the inorganic matrix, it is destined to impact fracture propagation. Thus, in this section, we elaborate on the mechanical qualities of kerogen and particularize the tools employed to measure them.

Estimating the kerogen’s mechanical characteristics constitutes an exacting process attributed primarily to the experimental challenges and uncertainty associated with the isolation of Kerogen. Given that the OM renders a lower stiffness compared to inorganic minerals, it influences fracture propagation in the course of reservoir stimulation and impacts the fracture closure behavior during reservoir depletion. In short, the mechanical properties, like hardness, toughness, tensile strength, compression failure, and creep characteristics, are a function of molecular structure and chemical composition.

Hardness is defined as the resistance of a material to penetration of a hard indenter when applying a prescribed force. Commonly, on a macroscopic scale, hardness is measured employing a Brinell indenter where the diameter of the indenter, a diameter of indentation, and the applied load are translated into a Brinell hardness number. The indenter is spherical with typical tests utilizing a 0.39 in steel ball as per ASTM E10–18. Conversely, Vickers and Knoop’s experiments implement microindentation hardness tests with indentation tests in the tenths of microns.

Given that the size of kerogen particles is in the order of a couple of hundreds of nanometers, none of the aforementioned indenter technologies is conducive to performing indentation tests on OM. Instead, kerogen mandates the application of nanoindentation techniques in the form of, for example, a Berkovich tip.

Historically, nanoindentation, also known as depth-sensing indentation and instrumented indentation, is frequently utilized to measure the mechanical qualities of thin films, coatings, or even smaller constituents. In addition to hardness measurements, the following properties can be obtained:

- Young’s modulus;
- Stress-strain relationship;
- Fracture toughness; and
- Plastic and elastic deformations.

Toughness is defined as the amount of energy per unit volume material can absorb before rupturing. Thus, toughness constitutes a bulk property related to fracture compression strength and tensile strength. Conversely, hardness is strictly a surface property seeking to estimate the resistance of a material to plastic deformation.

Indentation experiments for shales are of particular interest, given that they can be executed on easily available cuttings rather...
than costly core samples. Given that cuttings are usually comparatively small, the identification of the bedding orientation is difficult. This challenge was addressed by exploiting microindentation tests on artificial shale drill cuttings with random orientations.

The mechanical solutions acquired from isotropic and anisotropic materials are subsequently used to correlate the indentation modulus from randomly oriented cuttings to find the elements of the stiffness tensor for an isotropic material. The indentation modulus can be calculated drawing on elasticity theory, and it is equal to the plain strain modulus in isotropic samples. For all practical purposes, the indentation modulus is defined as the initial recovery of the indentation during the unloading stage.²

The testing procedure is initiated by positioning the indenter on top of the substance under investigation, as depicted in Figure 1. Next, the tips load and displacement are recorded during the loading and unloading stage. The residual depth of indentation may vary from nanometers to micrometers depending on the type of the material. The contact area at full load is determined by the depth of the impression and the known angle or radius of the indenter with hardness \( H \), being proportional to load \( P \) divided by the projected area of the contact surface \( A \). The shape of the unloading curve provides a measure of the elastic modulus.³

In order to obtain accurate mechanical measurements, it is paramount for the indenter tip to be perpendicular to the surface. Using sintered hydroxyapatite samples mounted individually to have indentation angles between 10° and 50°, where the 30° angle is evaluated as the critical one, Saber-Samadari et al. reported that the unloading curves have asymmetric residual impressions and elbow events when nonperpendicular surface penetration is performed.

Nanoindentation techniques can be divided into conventional and in situ nanoindentation approaches. The former indentation variant is also referred to as ex-situ nanoindentation, given that the nanoindenter is not attached to a microscope. Conversely, the in situ nanoindentation technique employs a microscope attached to the indenter to directly observe material behavior such as fracture propagation, fracture onset, and delamination.⁴

Subramani et al. categorized nanoindenter tips into four major types: Berkovich, cono-spherical, cube corner, and flat-end tips, with the Berkovich version being the most commonly used geometry. Notably, a cube corner tip is preferentially used to characterize the fracture toughness of materials. A cono-spherical tip captures the elastic-plastic transition contact and is suitable for both soft and hard materials. The flat-end tip is preferentially deployed for soft materials.

In terms of shales, nanoindentation also allows anisotropy to be measured if the bedding directions are known. According to Shukla et al., results for nanoindentation delineated Young’s modulus is in agreement with dynamic results, that is, values derived from acoustic techniques. Dynamic nanoindentation can be used for kerogen-rich shale samples to map the elastic moduli, aiding in detecting fine-grained constituents at greater resolution.

Several researchers sought to augment nanoindentation tools with a variety of modifications. Su et al. outlined an apparatus enabling the study of nanoscale mechanical behavior complemented by atomic force microscopy (AFM). Complementary to force spectroscopy, in tapping mode (TM), a technology exclusive to Bruker, AFM permits extending measurements beyond single indentations and elucidating mechanical properties in two dimensions.

With peak force tapping (PFT), piconewton (pN) force sensitivity became possible. In addition to high-resolution imaging, the technology allows for simultaneous quantitative property mapping of yield deformation (hardness), elastic modulus, adhesion energy, and energy dispersion. Liu et al. (2018) successfully applied statistical grid nanoindentation to estimate the mechanical properties of organic-rich shale samples.⁵ On top of offering nanoscale mechanical insights, the method overcomes the limitations of size requirements in the case of traditional triaxial mechanical tests that mandate inch-size core plugs. Similarly, massive grids of coupled wave dispersive spectroscopy (WDS) were employed along with instrumented indentation experiments to assess the composition and microstructure of shale at the microscale level.

Xu et al. exploited Fourier transform infrared (FTIR) and X-ray photoelectron spectroscopy (XPS) to uncover kerogen chemical composition and molecular structure, and AFM nanoindentation technology to investigate the adhesion and friction behavior. After cutting samples, argon ion polishing was performed, followed by SEM-EDS scanning. Subsequently, FTIR was deployed to determine the chemical elements’ bond by measuring the discrepancy of bond absorption. XPS is used in
the chemical molecular structure, determined by the peak position and shape. The work was complemented by micro-CT imaging to estimate the porosity.

A study by Eliyahu et al. sought to map the mechanical properties of organic and inorganic components using Peak Force Quantitative Nano-Mechanical (PF-QNM), a recent AFM mode derived from the PeakForce Tapping method. The method introduced in their work can help differentiate pyrite, quartz, clays, and organic matter by relating structural composition to mechanical properties. The cantilever deflection is used to elucidate the sample surface and the force curve produced. Subsequently, the elastic modulus is calculated by applying the Derjaguine-Muller-Toporov (DMT) model. The curve in Figure 2 is derived for each pixel, and parameters, including the reduced modulus, surface adhesion, and deformation, are estimated.

AFM-infrared spectroscopy (AFM-IR) can be applied to quantify OM’s mechanical and chemical heterogeneity in shale. An AFM probe with a constant tip was placed in an area that was simultaneously irradiated with a tunable wavelength IR laser. To observe how maturation affects nanoscale OM composition, samples at different stages of maturation were prepared using hydrolytic pyrolysis. This approach also allowed for examination of the evolution of OM during generation at the maceral level. In addition, the AFM-IR images were correlated with optical microscopy images to evaluate the mechanical and chemical properties of optically identifiable organic constituents.

Given the dispersed nature of kerogen in the shale matrix, measuring the compressive and tensile strength is challenging. Again, laboratory tests call upon nanocantilever beams to derive tensile strength features and strain-softening and hardening laws for kerogen-rich shales (KRS). The direct self-similar notched tension tests are commonly used to find macroscopic toughness and tensile strength properties. The dimensionless parameters, like the ratio of initial crack size over sample width and crack resolution, are used to characterize the notched tests. The toughness for linear elastic fracture mechanics (LEFM) is measured from high values of crack resolution segments.

Generally, there are three stages of creep: (i) primary creep, (ii) secondary creep, and (iii) tertiary creep. Primary creep is also recognized as a transient creep because the velocity of creep declines with time. Secondary creep is referred to as steady-state creep, given that in this state, the velocity is constant. Finally, tertiary creep is also called accelerating creep and is characterized by an increase in velocity with time. Importantly, tertiary creep indicates imminent sample failure.

3. NANO-MECHANICAL PROPERTIES OF ORGANIC RICH SHALES

Estimating the mechanical properties of kerogen experimentally is challenging, given that isolation of organic matter often mandates the application of strong acids. Even if successfully isolated, the mechanical properties may be altered due to demineralization-induced microstructure modifications. Nanoindenter-based measurements seek to overcome these limitations by measuring attributes in situ. Application of a nanoindenter necessitates, however, the sample to be polished, which may alter the mechanical characteristics. During indentation, forces applied are in the range of micro-Newton with the displacement in 100s of nanometers.

Rock tensile strength represents a crucial parameter when designing hydraulic fracturing treatments. There is evidence that the existence of kerogen in the shale matrix increases the tensile strength. Abousleiman et al. examined organic matter-rich Woodford shale samples by combining a nanoindenter with an SEM. Using FIB-SEM, nanocantilever beam structures were milled from the shale sample. The researchers noted that the amount of kerogen in the joining section of the nanocantilever beam impacts the stress—strain behavior. Brittle failure was observed for the tests conducted in kerogen-poor microcantilever beams. Conversely, both strain hardening and strain softening were observed before the beam failure under tension for the organic-rich specimen. Han et al. also reported a strain-softening behavior of kerogen under tensile failure in a microcantilever beam setting. Generally, the increase in tensile strength is attributed to the cross-linked nature of the polymers comprising the kerogen.

Likewise, Hull et al. (2015) studied the tensile failure of a microcantilever beam created in an organic-rich shale sample. The load—displacement curve was analyzed with the help of SEM imaging capturing initiation and propagation of fissures until failure. The elastic and plastic behavior was correlated with the amount of OM at the fracture surface. After failure, energy-dispersive X-ray spectroscopy (EDS) was used to analyze fracture faces and then establish a relationship between the mechanical behavior and composition. Hull et al. (2015) concluded that brittle and ductile behavior is positively correlated with high mineral and kerogen content, respectively.

A similar study was conducted using a shale sample from the Yanchang formation creating a microcantilever beam structure to inform crack propagation at the microscale. The study focused on observing the crack path and associated load—displacement curves. The microcantilever beams were prepared from different materials like kerogen, clay, and shale minerals. Figure 3 exemplifies the displacement curves obtained. Brittle failure was observed for beams devoid of organic material. In contrast, strain-hardening behavior was witnessed for beams containing kerogen. The authors noted different crack propagation behaviors such as crack deflection, branching, toughening in kerogen, and bridging.

Kerogen is well-known to provide softness to the rock matrix. Combining a nanoindenter with atomic force microscope (AFM) imaging, Zeszotarski et al. studied the hardness and modulus of kerogen parallel and perpendicular to the bedding plane. The organic matter was found to yield both elastic and
plastic behavior, rendering lower hardness values than any other shale constituent.

Exploiting nanoindentation, high-resolution maps of the elastic modulus of an organic-rich Bakken shale sample at the microscale were provided. It was found that the elastic modulus of kerogen is around 10 GPa, with clays exhibiting a modulus of 15—45 GPa depending on the particular type and orientation. Quartz is stiffest with an elastic modulus of 50—70 GPa. Abedi et al. analyzed the mechanical characteristics of a heterogeneous source rock rich in kerogen integrating EDX with a nanoindentation tool. They found kerogen to give rise to greater elasticity and a reduction in strength due to organic matter ductility.

Coupling creep nano- and microindentation with first-order modeling, a group of researchers found that organic matter greatly impacts shale rock creep rates. In contrast to the inorganic shale rock constituents, kerogen accelerates creep rates, causing a premature fracture conductivity reduction due to fracture closure and associated proppant embedment and, ultimately, a decreased production rate. Little information is available with respect to the temperature dependency of creep deformation. Working with oil shales, Eseme et al. concluded that temperature accelerates the creep deformation of organic-rich strata.13

4. KEROGEN MATURITY AND GEOMECHANICAL PROPERTIES

Isolating the effect of kerogen maturity on the mechanical properties on a macroscopic scale from primary sedimentary mineralogy, texture, and organic abundance constitutes a difficult task. Microfracture and nanoindentation methods are utilized to analyze samples, providing insight into the elastic properties at the basic component’s level.15 Combining AFM and IR spectroscopy, Abarghani et al. demonstrated that IR spectra could be used to quantify the maturity level of AFM based on Young’s modulus maps at the micron scale.16

Shukla et al. conducted a study integrating SEM with focus ion beam milling and nanoindentation to quantify the mechanical properties of Woodford shale-derived kerogen with varying maturities. SEM with EDS was used to identify the kerogen presence, while an ion beam was employed to create grooves surrounding the kerogen. It was observed that Young’s modulus and hardness were inversely related to porosity, clay content, and, predominately, kerogen presence. In addition, the researchers noted that local porosity and organic matter type influenced the kerogen’s mechanical properties.

AFM-infrared spectroscopy (AFM-IR) was exploited to quantify organic matter’s mechanical and chemical heterogeneity in shale. Simulating different stages of thermal maturation through the hydrous pyrolysis technique, they concluded that maceral composition controls the mechanical properties. For example, macerals enriched with aromatic carbon yield a comparatively higher stiffness.

Khatibi et al. (2018) linked Rock-Eval pyrolysis and vitrinite reflectance, %Ro, derived maturity values with Raman spectroscopy measurements. The established correlation suggested a positive relationship between the organic matter’s Young’s modulus, as derived by PeakForce AFM, and its maturity level-dependent Raman response. Similarly, Abedi et al. showed that the mechanical properties of organic-rich shales are associated with their maturity level and organic content.

Exploiting scanning acoustic microscopy, Prasad et al. correlated the acoustic response of organic matter with the maturity level. The authors concluded that the heterogeneity of texture, velocity, density, and elastic impedance increases as the maturity advances. Other authors substantiated the results of alternative techniques like nano dynamics mechanical analysis and AFM.17

5. CLAY INTERBEDDED KEROGEN AND GEOMECHANICAL PROPERTIES

Quantifying the elastic characteristics of clays is crucial to reconcile the response of seismic and sonic logs of shales and inform hydraulic fracturing design. Even in the absence of organic matter, however, shales yield anisotropic mechanical properties due to their bedding planes, the presence of heterogeneous minerals, and microcracks. Vernik et al. showed that the interbedding between clay and kerogen introduces additional anisotropy (see Figure 4).13 Consequently, two shale samples with the same clay content may have different elastic properties because of varying clay distribution.

As with kerogen, it is difficult to isolate clay grains to measure their properties directly. Hence, measurements may need to be executed at the nanoscale or substituted by exploiting computational modeling techniques. Utilizing nanoindentation, Liu et al. (2018) concluded that the presence of clay in Bakken shale samples reduced both the rock hardness and Young’s modulus. Combining molecular simulation with nanoindentation experiments for montmorillonite, Pal-Bathija recognized that the interlayer water content has a considerable influence on the mechanical properties.

Applying PF-QNM, Li et al. investigated the chemomechanical properties of organic matter and clays of immature Bakken shale. The elastic modulus was found to be between 2 to 6 GPa. For clays only, the elastic modulus ranged from 7 to 20 GPa.17

6. ATOMIC MODELING OF KEROGEN GEOMECHANICS

The in situ assessment of mechanical properties is exceedingly difficult given the dispersed nature of kerogen. Similarly, the extraction of kerogen in sufficient quantities for experimental characterization is rather laborious and may require the application of strong acids.

Alternatively, kerogen molecules can be represented virtually, allowing for computational-based studies of their mechanical qualities. The computational approach has been applied successfully for materials of similar nature like polymers. Like
kerogens, polymers are composed of carbon–carbon and carbon–hydrogen bonds constituting the backbone of the molecule. Estimated mechanical properties of polymers revealed a reasonable agreement with experimentally obtained data making researchers confident in extending the approach to other materials.17

The governing principle of the approach consists of recreating a representative molecular or macromolecular unit and configuring force field centers, their types, and charges. Next, an amorphous structure consisting of a number of units is assembled. During this stage, it is vital to ensure having a representative elementary volume and consistent macroscopic properties like density and porosity. Finally, the structure is deformed in a prespecified direction, and its energy is quantified before and after deformation. The result is translated into a stiffness matrix that can be solved to yield the mechanical property of interest. A summary of the steps is given in Figure 5.

A critical part of the process is the identification of molecular force centers. A given molecule could have a single or multiple force center. The choice is made depending on the complexity and the size of the molecule. Kerogens consist of large macromolecular units and, hence, atoms within the same unit are treated as force centers with specified charges. Force fields have been established to facilitate the identification of force centers and the assignment of charges. For organic-based compounds like kerogen and force fields such as COMPASS and CFF93 were introduced to facilitate molecular simulation processes.18 Sun and Sun et al. Complementing the aforementioned force fields, the polymer-consistent force fields PCFF and PCFF+ were introduced to cover a wider range of elements. Parameterization of kerogen macromolecules using PCFF+ has been proven adequate to reproduce experimentally measured properties.19

Upon force field parametrization of the macromolecules, amorphous structures of representative size are formed from the individual units using a molecular dynamics approach. The process consists of several stages, including velocity initialization, an isochoric-isothermal NVT ensemble, and an isobaric–isothermal NPT ensemble. The molecular interactions are governed by the Lennard-Jones 9–6 potential with Waldman and Hagler mixing rules for unalike force centers. Simulation temperature, pressure, running time, and other parameters are selected to ensure that the final structure matches experimentally delineated properties.

The structure is deformed by redefining the lattice vector \( L = (a_1, a_2, a_3) \) to a disturbed cell \( L' = (a'_1, a'_2, a'_3) \), applying a strain matrix:20

\[
L' = L \begin{pmatrix}
1 + \varepsilon_{xx} & \frac{1}{2} \varepsilon_{xy} & \frac{1}{2} \varepsilon_{xz} \\
\frac{1}{2} \varepsilon_{yx} & 1 + \varepsilon_{yy} & \frac{1}{2} \varepsilon_{yz} \\
\frac{1}{2} \varepsilon_{zx} & \frac{1}{2} \varepsilon_{zy} & 1 + \varepsilon_{zz}
\end{pmatrix}
\]

(1)

The total energy of the system can then be calculated as

\[
U = \frac{E_{\text{tot}} - E_0}{V_0} = \frac{1}{2} \sum_{i=1}^{6} \sum_{j=1}^{6} C_{ij} \varepsilon_{ij}
\]

(2)

where \( U \) is the stress per unit volume, \( V_0 \) is the initial volume of the cell, \( E_0 \) is the energy of prior deformation, \( E_{\text{tot}} \) is the energy after deformation, and \( C_{ij} \) is the element of the stiffness matrix.

In order to explicate mechanical properties, stepwise incremental strains are enforced to obtain a stress–strain relationship. The linear portion of the stress–strain relationship is exploited to deduce the elastic constants, and the nonlinear domain informs the nature of plastic deformation kerogen failure. This general workflow was successfully applied to kerogen, delineating the factors influencing the geomechanics,21 studying the interface between clay and organic materials, and the role of the contained fluid on the mechanical behavior of kerogen matter.
7. KEROGEN AND HYDRAULIC FRACTURING

Over the past decade, petroleum production from organic rich shale reservoirs became more economical due to technological breakthroughs in the oil and gas industry and due to the improvements implemented in hydraulic fracturing in particular. Organic rich shales are composed by several minerals such as clay, quartz, and carbonate along with organic matter (kerogen). Kerogen is one of the main constituents of mud rocks in organic rich shales such as formations in Barnett, Woodford, EagleFord, and Marcellus basins in the U.S. Thoroughly understanding the mechanical properties of the mud rocks is essential in developing and optimizing hydraulic fracturing procedures in any shale formation. Understanding and capturing the impacts of the different kerogen mechanical properties will play a major role in improving the efficiency of hydraulic fracturing and therefore improve the low recovery factor of shale reservoirs.

For a capital-intensive procedure such as hydraulic fracturing where tensile failure is generated within the rocks, proper design is required to optimize production and make such a process economically worthwhile. Essential understanding of the geomechanics and especially the brittleness of the rocks is one of the main requirements to generate a successful hydraulic fracturing job. Kerogen has lower stiffness than inorganic minerals which affects the initiation and propagation of fractures in kerogen-rich formations. The main means to estimate the brittleness of kerogen are the Young’s modulus and Poisson’s ratio.

7.1. Brittleness Index and the Impact of Kerogen.

Brittleness index (BI) is used to quantify brittleness which characterizes possible failures in rock. The stress-strain curves of loading and failure are used to reflect brittle vs ductile behavior of materials as shown in eq 3:

\[ BI = \frac{E_{el}}{E_{tot}} \]  

(3)

where \( E_{el} \) the elastic (recoverable) strain and \( E_{tot} \) is the total strain at failure. The stress-strain curve parameters are stresses and strains, Young’s modulus, Poisson’s ratio, and pre- and postpeak energy balance. These parameters calculate brittleness precisely in the laboratory. However, test practices are expensive and time consuming. Zhang et al. (2016) reviewed more than 22 methods to find BI. For example, BI can be found by continuously absorbing energy before failure, longitudinal strain, and shear strength-based brittleness. Also, Young’s modulus and Poisson’s ratio are used to find BI. To evaluate the drill ability, direct methods to quantify BI are penetration, impact, and hardness tests. Infield applications BI s based on mineral composition and Young’s modulus are used.

Aoudia et al. introduced a method in 2010 to find brittleness using multivariate statistical analysis. This method can relate 36 parameters, including: TOC, rock mechanical properties, and geochemical data. The analysis revealed that Young’s modulus and Poisson’s ratio are strongly affected by quartz and clay content. However, TOC showed a small effect on this modulus. Some results regarding brittleness and frack-ability of the upper, middle, and lower Woodford shale are determined in this research. The data are modeled to fracturing material to see the different fracturing scenarios, and then the results are compared to the statistical analysis performed. The rock mechanical multivariate statistical analysis somewhat demonstrates the hydraulic fracture modeling results.
Table 3. Summary of Kerogen Properties Derived from Simulation

| property                  | method                                                                 | sample origin and maturity                                                                 | typical values                                                                 | remarks                                                                                                                                                                                                 |
|---------------------------|------------------------------------------------------------------------|---------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| link petro-physical       | 8 units of nanoporous kerogens with final structure formed using MD   | the modeling results were compared to experimental data for Woodford and Kimmeridge shale   | At 6% porosity $E = 2.2$ GPa, $G = 0.8$ GPa, $K = 3.5$ GPa, and $\nu = 0.4$; while at 20% $E = 1$ GPa, $K = 0.9$ GPa, $G = 0.3$ GPa, and $\nu = 0.32$ | the lower viscosity kerogen had the highest elasticity, the mechanical behavior is affected by temperature and pore fluids |
| properties of kerogen     | thermodynamic technique was created to predict Kerogen fracture properties which are validated with experimental data |                                                                               | KIC interface / KIC matrix = 0.7, elasticity of kerogen = 10 GPa               | the kerogen and kerogen-silica show ductility, the component’s ductility reduces the shale ductility, even with ductile inclusions | toughness, ductility, and elasticity |
| to its mechanical properties (E, K, G, (v)) |                                                                      |                                                                               |                                                                               |                                                                                                                                                                                                 |
| Britteness, density,      | 8 units of nanoporous kerogens with final structure formed using MD   | the modeling results were compared to experimental data for Woodford and Kimmeridge shale   | at 6% porosity $E = 2.2$ GPa, $G = 0.8$ GPa, $K = 3.5$ GPa, and $\nu = 0.4$; while at 20% $E = 1$ GPa, $K = 0.9$ GPa, $G = 0.3$ GPa, and $\nu = 0.32$ | the lower viscosity kerogen had the highest elasticity, the mechanical behavior is affected by temperature and pore fluids |
| Young’s modulus,          | thermodynamic technique was created to predict kerogen fracture properties which are validated with experimental data |                                                                               | KIC interface / KIC matrix = 0.7, elasticity of kerogen = 10 GPa               | the kerogen and kerogen-silica show ductility, the component’s ductility reduces the shale ductility, even with ductile inclusions | toughness, ductility, and elasticity |
| and Poisson’s ratio       |                                                                                                                                     |                                                                               |                                                                               |                                                                                                                                                                                                 |
| elastic moduli            | apparent isotropic definitions, exact anisotropic formulation and approximate anisotropic expressions for weak VTI anisotropy | the model calibrated to the black shales of the Bakken formation (Williston basin)       | $K$ varied between 7 and 13 GPa, $\nu$ between 0.2 and 0.3, $E$ between 10 and 20 GPa, and $G$ between 4 and 7.5 GPa | Young’s modulus had excellent agreement between the different approaches unlike Poisson ratios |
| mechanical moduli,        | atomicistic modeling                                                    | kerogen type II with maturity varies from immature to overmature                      | $K$ varied between 7 and 13 GPa, $\nu$ between 0.2 and 0.3, $E$ between 10 and 20 GPa, and $G$ between 4 and 7.5 GPa | a Poisson’s ratio estimate for kerogen across densities and maturities |
| compressive, and          | this investigation macromolecules; the kerogen macromolecules are tailored to the H/C, O/C, and N/C ratios, average aromaticity, and average aromatic unit size | kerogen type I used three kerogen II and III                                           | for type I cohesion was 42.8 MPa, friction coefficient 0.161, for 1 atmospheric pressure the tensile strength 72.9 MPa, and compressive strength 100.1 MPa, $\nu = 0.24$ $E = 1.5$ GPa (from a table) | due to its lower mechanical properties, kerogen may be the location of fracture initiation, the kerogen has lower Young’s modulus than shale minerals; its compressive strength is less than that of brittle rocks |
| tensile strengths         |                                                                                                                                     |                                                                               |                                                                               |                                                                                                                                                                                                 |
The brittleness based on Young’s modulus and Poisson’s ratio characterize the original physical properties of reservoirs, while the mineral brittleness considers the mineral volume in the shale and brittle factor of every single mineral. They both can explain reasonably the brittleness of rocks from logging and prestack seismic inversion. Mineral elastic parameter factor was established to calculate the elastic parameters of high quality brittle from logging data. This is performed based on the rock physics model of organic-rich shale.\(^{23}\)

### 7.2. Impact of Kerogen in Brittleness Index

Shale is composed of a variety of minerals having different brittleness, kerogens are characterized as nonbrittle minerals. The effect of kerogen and other factors were investigated in terms of anisotropy. The elastic modulus (bulk modulus and shear modulus) of kerogen is considered to be relatively low in kerogens which is the case with clay too having a lower P-wave velocity, S-wave velocity, and density than the surrounding rock. Kerogen along with pore geometry proved to have a significant impact on the elastic properties.

Given that ductile matters (nonbrittle) such as organic matter and clay minerals tend to diminish brittle rock characteristics while brittle minerals such as quartz and carbonate minerals tend to promote rock brittleness, the following method is established to express the impact of rock mineral components in brittleness index as shown in eq 2.

\[
BI = \frac{w_b}{w_b + w_d}
\]

where \(w_b\) is the weight fraction of brittle minerals and \(w_d\) is the weight fraction of ductile minerals.\(^{24}\)

Organic matter in shale tend to have higher porosity and permeability than surrounding rock matrix. This would provide pores for the reservoir and flow channels of fluids. Furthermore, pores could be formed between matrix and organic matter due to the volume shrinkage of the OM. These factors would have a direct effect on hydraulic fracturing. With regard to the shale mineral compositions, the higher content of brittle minerals and lower content of clay minerals can lead to higher shale brittleness and therefore a greater fracturing availability.

### 7.3. Hydraulic Fracturing Challenges in the Presence of Kerogen

The presence of kerogen due to its nonbrittle nature, would lead to several challenges in conducting a successful hydraulic fracturing job. Therefore, addressing these challenges and resolving them is critical to optimize stimulation and make it economically feasible to conduct hydraulic fracturing in organic-rich shale.

Methods of composition and systems for degrading OM like kerogen in subterranean formation increase the efficiencies of hydraulic fracturing in unconventional formations. There are several methods such as treating kerogen using oxidizers (persulfate and bromate). The presence of ductility and the polymer nature of kerogen have made hydraulic fracturing challenging. OM is intertwined among minerals like aluminosilicates, and silicates as fine laminae add soft mechanical cohesion to shale rocks. Strong oxidizers (that is, Bromate \(BrO_3^-\)) as part of a new type fracturing fluid is developed to be a potential solution that lessens the adverse effects of kerogen’s polymeric nature on the hydraulic conductivity of fractured shales. Kerogen-rich shale samples were imaged using high-resolution SEM before and after fluid treatment. This showed porosity improvement proven by the formed cracks in macerals and augmenting volumetric porosity.\(^{25}\)

Hydraulic fracturing fluid selection is critical in any stimulation job and plays a major role in the success of these highly costly procedures.\(^{25}\) We have presented quantitative evidence for kerogen alteration when exposed to hydraulic fracturing fluid. Since kerogenic pore networks are the dominant pathways of hydrocarbon transport in shale reservoirs, hydrophilic behavior would reduce the transport of hydrocarbons through the organic pore network. It is believed that kerogen plays a major role as a contaminant source in shale reservoirs.

### 8. RECOMMENDATIONS AND FUTURE WORK

The nanoscale research area on kerogen’s mechanical properties is new and has potential for further understanding. Most of the experimental research was applied to kerogen contained within a shale sample. It could be of great interest to measure the mechanical properties of isolated kerogen to separate the impact of rock grains and cement. Kerogen has many types, as illustrated in this study and the literature; nevertheless, there are no reports of the mechanical properties of each type. Fluids interact with kerogen during hydraulic fracturing, and research on the impact of such interactions on kerogen strength is important. Atomistic modeling of kerogen could reveal knowledge that cannot be demonstrated experimentally. For instance, kerogen composition at the atomic level could be varied to see which compositions contribute more to the softness and hardness of kerogen. Also, fluid interactions with kerogen such as CO\(_2\) and how they mechanically alter kerogen are more feasible through molecular dynamic simulations.

### 9. SUMMARY

Research in unconventional reservoirs necessitates understanding of the mechanical properties of kerogen. Nevertheless, kerogen exists as aggregates within the rock fabric, resulting in challenges in understanding its unique properties. Advances in experimental tools at the nanoscale made it possible to understand kerogen’s mechanical behavior despite its attachment to the rock grains. Also, molecular dynamic simulations enabled simulation of kerogen’s mechanical behavior and its stress-strain response. The geo-mechanical properties that were used to characterize the kerogen are brittleness, stress, strain, elastic moduli, and hardness. Different methods are used to find the moduli, including SEM equipped with nanoindentor and Raman Spectroscopy including an AFM. However, PFIR microscopy can be used to find the chemical composition, aromaticity, and adhesion which can later be linked to the mechanical properties.

Kerogen is also characterized by its lower stiffness and hardness compared to the rock matrix. At the same time, it has higher tensile strength due to the cross-linked nature of the polymers comprising the kerogen. It is also known to accelerate the rock creeping due to stress, especially when interbedded with clay. Interestingly, kerogen maturity was shown to influence its mechanical properties significantly. The advancement in the experimental and molecular simulation research are summarized in Tables 2 and 3.

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The manuscript was written through contributions of all authors.

Notes

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References

(1) Hutton, A.; Bharati, S.; Robl, T. Chemical and Petrographic Classification of Kerogen/Macerals. Energy Fuels 1994, 8, 1478−1488.
(2) Vandenbroucke, M.; Largeau, C. Kerogen origin, evolution and structure. Org. Geochem. 2007, 38, 719−833.
(3) Khatibi, S.; Aghajanpour, A.; Ostadhassan, M.; Ghanbari, E.; Amiran, E.; Mohammad, R. Evaluating the Impact of Mechanical Properties of Kerogen on Hydraulic Fracturing of Organic Rich Formations. Society of Petroleum Engineers. SPE Canada Unconventional Resources Conference, URC 2018 2018, March, 13−14.
(4) Alstadt, K. N.; Katti, K. S.; Katti, D. R. Nanoscale Morphology of Kerogen and In Situ Nanomechanical Properties of Green River Oil Shale. J. Nanomech. Micromech. 2016, 6, 04015003.
(5) Martogi, D.; Abedi, S. Indentation Based Method to Determine the Mechanical Properties of Randomly Oriented Rock Cuttings, 3rd US Rock Mechanics/Geomechanics Symposium, New York City, NY, 2019.
(6) Hainsworth, S. V.; Chandler, H. W.; Page, T. F. Analysis of nanoindentation load displacement loading curves. J. Mater. Res. 1996, 11, 1987−1995.
(7) Rojewiejska-Malyk, K.; Mook, W.; Parlinska-Wojtan, M.; Hejduk, J.; Michler, J. In situ scanning electron microscopy indentation studies on multilayer nitride films: Methodology and deformation mechanisms. J. Mater. Res. 2009, 24, 1208−1221.
(8) Liu, K.; Ostadhassan, M.; Bubach, B.; Ling, K.; Tokhmechi, B.; Robert, D. Statistical grid nanoindentation analysis to estimate macro-mechanical properties of the Bakken Shale. J. Nat. Gas Sci. Eng. 2018, 53, 181−190.
(9) Elyahu, M.; Emmanuel, S.; Day-Stirrat, R. J.; Macaulay, C. I. Mechanical properties of organic matter in shales mapped at the nanometer scale. Mar. Pet. Geol 2015, 59, 294−304. 450
(10) Hull, K. L.; Abousleiman, Y. N.; Han, Y.; Al-Muntasheri, G. A., Hosemann, P.; Scott Parker, S.; Howard, C. B. New Insights on the Mechanical Characterization of Kerogen-Rich Shale, KRŠ. Society of Petroleum Engineers—Abu Dhabi International Petroleum Exhibition and Conference, ADIPEC2015, DOI: 10.2118/177628-MS.

(11) Zhao, J.; Zhang, D. Dynamic microscale crack propagation in shale. Eng. Fract. Mech 2020, 228, 106906.

(12) Esfahani, E.; Urai, J. L.; Kroos, B. M.; Littke, R. Review of mechanical properties of oil shales: Implications for exploitation and basin modelling. Oil Shale 2007, 24, 159.

(13) Mason, J.; Carloni, J.; Zehe, A.; Baker, S. P.; Jordan, T. Dependence of Micro-Mechanical Properties on Lithofacies: Indentation Experiments on Marcellus Shale. Society of Petroleum Engineers SPE/AAPG/SEG Unconventional Resources Technology Conference 2014, DOI: 10.15530/URTEC-2014-1922919.

(14) Abarghani, A.; Ostadhassan, M.; Hakley, P. C.; Pomerantz, A. E.; Nejati, S. A chemo-mechanical snapshot of in-situ conversion of kerogen to petroleum. Geochim. Cosmochim. Acta 2020, 273, 37–50.

(15) Vernik, L.; Nur, A. Ultrasonic velocity and anisotropy of hydrocarbon source rocks. Geophysics 1992, 57, 727–735.

(16) Li, C.; Ostadhassan, M.; Kong, L. Nanochemical-technological characterization of organic shale through AFM and EDS. SEG Technical Program Expanded Abstracts 2017, 3837–3840.

(17) Theodorou, D. N.; Suter, U. W. Atomistic modeling of mechanical properties of polymeric glasses. Macromolecules 1986, 19, 139–154, DOI: 10.1021/ma00155a022.

(18) Sun, H. COMPASS: An ab Initio Force-Field Optimized for Condensed-Phase Applications Overview with Details on Alkane and Benzene Compounds. J. Phys. Chem. B 1998, 102, 7338–7364.

(19) Ungeer, P.; Coltell, 478 J.; Yiannourakou, M. Molecular Modeling of the Volatlic and Thermodynamic Properties of Kerogen: Influence of Organic Type and Maturity. Energy Fuels 2015, 29, 91–105, DOI: 10.1021/ef502154k.

(20) Walpole, L. J. On bounds for the overall elastic moduli of inhomogeneous systems-II. J. Mech. Phys. Solids 1966, 14 (5), 289–301.

(21) Alafnan, S. The Impact of Pore Structure on Kerogen Geomechanics. Geofluids, 2021.

(22) Bokhonok, O.; Ravazzoli, C. The influence of kerogen content on some brittleness indicators in a rich organic shale—Comparative analysis of different approaches. VIII Simposio Brasileiro de Geofísica (SBGF), Ouro Preto, 2016 DOI: 10.22564/4117SIMBGF2016.185.

(23) Liu, Z.; Sun, Z. New brittleness indexes and their application in shale/clay gas reservoir prediction. Petroleum Exploration and Development 2015, 42, 129–137.

(24) Ye, Y.; Tang, S.; Xi, Z. Brittleness Evaluation in Shale Gas Reservoirs and Its Influence on Fracability. Energies 2020, 13, 388 DOI: 10.3390/EN13020388.

(25) Hull, K. L.; Jacob, D.; Abousleiman, Y. N. Oxidative Kerogen Degradation: A Potential Approach to Hydraulic Fracturing in Unconventionals. Energy Fuels 2019, 33, 4758–4766.