Assessment of the Multiphase Mechanical Properties of the Longmaxi Formation Shale Using Nanoindentation Tests

Yunqian Long,* Ya Zhang, Xiaohe Huang, Yuyi Wang, Yanhong Zhao, Renyi Wang, and Fuquan Song

ABSTRACT: Mechanical properties are some of the most important parameters for understanding well drilling and hydraulic fracturing designs in unconventional reservoir development. As an effective tool, nanoindentation has been used to determine the mechanical properties of rocks at the nanoscale. In this study, the Longmaxi Formation shale samples from the Yibin area of China were collected and analyzed to obtain the multiphase mechanical properties. The mineral compositions and organic geochemistry of the shale samples were studied using X-ray diffraction, energy-dispersive X-ray spectrometry, and a carbon/sulfur analyzer. The pore structures of the shale samples at the micro- and nanoscales were characterized by field-emission scanning electron microscopy. The mechanical parameters of the shale samples, such as the hardness and elastic modulus, were investigated using the nanoindentation method to identify three mineral phases: brittle minerals, soft matters, and complex minerals at the interfaces between brittle minerals and soft matters. The uncertainty characteristics of the mechanical parameters of the three mineral phases were evaluated using the Weibull model, and the factors interfering with the mechanical parameters were analyzed for the different shale samples. The results showed that the brittle minerals had the largest recovered elastic deformations and the smallest residual deformations, while the soft matters had the largest residual deformations and the smallest recovered elastic deformations. The analysis results of the coefficients of variation and the Weibull modulus both confirmed that the scatter of the hardness was higher than that of the elastic modulus because of the uncertain contact area, and the hardness and elastic modulus of the soft matters had the highest uncertainty among the three mineral phases. The elastic modulus increased nonlinearly with increasing hardness according to a power function for the whole shale sample. The elastic modulus and hardness both had a favorable linear relationship with the total organic carbon (TOC) content, illustrating that the TOC content was one of the significant factors that affected the mechanical parameters of the shale samples.

1. INTRODUCTION

Because of the rapid progress of hydraulic fracturing and horizontal drilling technology, the exploration and development of shale gas reservoirs have achieved great commercial success over the past decade,1 and a considerable increase in gas production has been achieved.2 Shale is a strong heterogeneous sedimentary rock with complex mineral compositions and pore structures. The mechanical properties of shale have a noticeable anisotropy at the macroscale and exhibit strong heterogeneity at the microscale.3 Thus, it is difficult to correctly measure the mechanical properties of shales. Usually, macroscale experiments, such as uniaxial and triaxial tests, are carried out on shale samples to quantify the mechanical parameters of shale samples.4,5 However, these macroscale experiments require bigger and more complete core samples with the diameter ranging from 2.5 to 5 cm and the height in the range of 2.5—10 cm, which are difficult to obtain because of the limitation of the sampling position.6 In addition, these methods have the disadvantages of high costs, long experimental periods, and low precision.6,9 Moreover, it is difficult for macroscale analysis to reveal the elastoplastic deformation behavior and to explain the anisotropy and complexity that occur in the course of hydraulic fracturing because the micro- and nanoscale heterogeneities are not considered.10 The macroscale mechanical characteristics of shales are closely related to their microscale mechanical properties.11 The quantitative characterization of microscale mechanical properties can provide information for further research on the propagation and evolution of fractures and the formation mechanism of complex fracture networks.12,13 Therefore, recently, many researchers have devoted their efforts...
to determining the mechanical properties of shales at the micro- and nanoscales.

The limitations of the macroscale experiments have promoted the development of novel micro- and nanoscale measurement methods.14 The nanoindentation technology was carried out in the 1980s to determine the mechanical properties of homogeneous materials such as metals, films, and crystals.15,16 and now, it is one of the most common techniques for studying mechanical properties and analyzing the elastic–plastic transition.17 Nanoindentation tests can be applied to determine the mechanical parameters of materials at the micro- and nanoscales, including the elastic modulus, hardness, scratch, and creep.18 Because nanoindentation tests can be carried out on millimeter-scale samples, the required shale samples are more easily obtained and prepared from drilling debris and wellbore debris.19 Thus, the nanoindentation technology shows promise in estimating the mechanical properties of coals and shales at the micro- and nanoscales.

Numerous researchers have investigated the mechanical properties of coals and shales at the microscale using the nanoindentation method.20–22 Zhang et al. studied the nanomechanical properties of different rank coals23 and the nanoscale mechanical property variations in heterogeneous water absorbing coal.24 They found that the elastic modulus exhibited an increasing tendency from low- to high-rank coal, and compared with the traditional acoustic tests, the nanoindentation tests could correctly measure the variations in the rock mechanical properties for the heterogeneous water absorbing coal. Chen et al. analyzed the mechanical properties of Longmaxi Formation shale samples using microindentation tests and evaluated the relationships between the macro- and mesoscale mechanical properties of shale samples.25 The results showed that the mesoelastic modulus and the mesohardness were inhomogeneous, and the statistical average value of the mesoscopic elastic modulus was consistent with the value of the macroscopic elastic modulus. Li and Ostadhassan used the nanoindentation method to quantify the nanoscale mechanical properties of Bakken shale samples and found that Bakken shale samples have a lower average Young’s modulus and hardness, and there is a positive relationship between Young’s modulus and hardness.26 Shi et al. studied the mechanical properties of Longmaxi Formation shale samples with vertical and parallel bedding through the measurement method of dot matrix nanoindentation and then upscaled the mechanical parameters from the nanoscale to the centimeter scale using the Mori–Tanaka model.27 Their results revealed that the elastic modulus, hardness, and fracture toughness of the shale samples with vertical bedding were a little lower than those of the shale samples with parallel bedding. By comparing the results of nano-, meso-, and macroscale tests, they found that the mechanical parameters at the nanoscale were higher than those at meso- and macroscales, which indicated that the mechanical parameters had scale differences. Manjunath and Jha used the nanoindentation method to analyze the mechanical properties of Gondwana shale samples at nano- and microscales and investigated the effect of the multiphase mineralogical properties at nano- and microscales on fracture propagation at the mesoscale.14 However, the majority of these studies focused on the effects of scale changes to the mechanical properties of shale samples. As a sedimentary rock with strong heterogeneity, shale has very complex mechanical properties because of the presence of various mineral phases, such as quartz, feldspar, calcite, and clay minerals. These various mineral phases will inevitably have a serious influence on the mechanical properties of shale samples.28 However, how the various mineral phases affect the mechanical properties of shale samples is still poorly understood. Thus, it is essential to investigate the mechanical properties of the various mineral phases in shale samples in detail and to probe the mechanisms affecting the mechanical properties in depth.

In this study, to further our understanding of the mechanical properties of the different mineral phases in shale samples at the nanoscale, the Longmaxi Formation shale samples from the Yibin area were collected and characterized using X-ray diffraction (XRD), energy-dispersive X-ray spectrometry (EDX), and field-emission scanning electron microscopy (FE-SEM). Then, the mineral compositions of the shale samples were divided into three mineral phases: brittle minerals, soft matters, and complex minerals at the interfaces. The mechanical parameters of these three mineral phases, such as the hardness and elastic modulus, were determined using the nanoindentation method and were further analyzed to evaluate the uncertainty characteristics using the Weibull model. Finally, correlative relationship analyses were conducted between the mineralogy and geochemistry and the hardness and elastic modulus of the different shale samples. This study will enable us to better understand the effects of mineralogy on hydraulic fracturing.

2. EXPERIMENTAL SECTION

2.1. Sample Preparation. Six Longmaxi Formation shale samples, 25 mm in diameter and 50 mm in length, were collected from the Yibin area and were analyzed to determine their mineral compositions, geochemical and microstructure characteristics, and micromechanical parameters. A part of each shale sample was cut and processed (25 mm in diameter and 10 mm in length) for the nanoindentation tests. The pore structure measurements of two shale samples were carried out on a high-resolution FE-SEM. For mineral composition determinations, the rest of each shale sample was crushed to 400-mesh fine powder, mounted into a sample container, and measured on a D8 DISCOVER XRD instrument with a counting time of 20 s, a scanning speed of 2° (2θ)/min, a step width of 0.02° (2θ), and a scanning range from 5° to 90° (2θ). For total organic carbon (TOC) content measurements, 400-mesh shale samples were treated with hydrochloric acid to remove carbonates, washed with deionized water, dried for 24 h at 70 °C, and were measured using a Leco CS844 carbon/sulfur analyzer.

2.2. Field-Emission Scanning Electron Microscopy. The micromorphological and structural characteristics of two shale samples with different TOC contents were determined using FE-SEM. First, 1 cm × 1 cm shale sections were prepared and polished using mechanical grinding to generate a smooth surface. Then, the polished surface had been argon-ion-milled for 3 h to obtain an ultrasmooth surface at an ion beam incidence angle of 3° and a voltage of 5 kV using a Leica EM TIC 3X ion beam milling system. After this, the surface was observed using a Hitachi SU8010 high-resolution FE-SEM.

2.3. Nanoindentation. Nanoindentation has been widely applied to determine mechanical parameters, such as the elastic modulus and hardness, which has demonstrated that it is a significant method for determining the mechanical properties of rocks at smaller scales.29 A single nanoindentation experiment involves three stages: the loading stage, the holding stage, and the unloading stage. First, the indenter is pressed into the surface of the rock according to the determined loading rate. Then, the
load is maintained for a certain amount of time to eliminate measurement errors when it reaches the maximum value. After that, the load is gradually reduced to 0 within the specified time according to a certain unloading rate. The rock generates elastic deformation when the indenter enters into the surface of the rock. Then, as the load is increased, the rock starts to produce plastic deformation, and an indentation with the shape of the indenter can be observed. When the unloading stage starts, the elastic deformation is restored and the plastic deformation leaves an indentation, as shown in Figure 1a. The load–displacement curve can be plotted according to the experimental data and can be applied to calculate the hardness and elastic modulus of the rock, as shown in Figure 1b.

The Oliver and Pharr method\(^\text{30}\) has been applied to compute the hardness and elastic modulus through fitting an unloading curve using a power function to obtain two parameters: the hardness and elastic modulus of the Berkovich indenter. Therefore, Young’s modulus of the rock can be computed using eq 7:

\[
\frac{1}{E_i} = \frac{1 - v_i^2}{E} + \frac{1 - v_r^2}{E_r}
\]

where \(E\) is Young’s modulus of the rock, \(v\) is Poisson’s ratio of the rock, \(v_i\) is Poisson’s ratio of the Berkovich indenter, and \(E_i\) is the elastic modulus of the Berkovich indenter. \(E_i\) is 1140 GPa and \(v_i\) is 0.0717\(^\text{17}\) for the Berkovich indenter.

### 2.4. Experimental Nanoindentation Procedures

The surfaces of six shale samples (25 mm in diameter and 10 mm in length) were mechanically polished using abrasive papers with different grits (from 400 to 1200 grit), and then 1 cm × 1 cm shale sections were prepared from the above shale samples and had been argon-ion-milled for 3 h to obtain ultrasmooth surfaces at an ion beam incidence angle of 3° and a voltage of 5 kV using a Leica EM TIC 3X ion beam milling system. Figure 2 shows the prepared samples for the nanoindentation test.

shale samples after the milling for the nanoindentation tests. Figure 3a,b shows the 3D and 2D tomography of sample 3 obtained by a Dimension ICON atomic force microscope, respectively. The roughness for sample 3 was about 200 nm, which fulfilled the flat surface requirement of nanoindentation. The nanoindentation tests were carried out on an Anton Paar TTX-NHT3 nanoindenter with a load resolution of 40 nN, a maximum load of 500 mN, a maximum depth of 200 \(\mu\)m, and a displacement resolution of 0.04 nm in the \(z\)-direction. The indenter used in the experiments was a Berkovich indenter shaped like a triangular pyramid. All of the load-controlled indentation tests were implemented with a constant loading rate of 16 mN/s and a constant maximum load of 500 mN. The load was increased with time in a linear manner until the maximum load was reached, and then, the force was maintained constant at the maximum indentation for 10 s before the indenter was linearly unloaded with time. To avoid the effect of adjacent measuring points, the distance between each measuring point was greater than 60 \(\mu\)m. The 90 nanoindentation points for each sample were set to carry out the indentation tests. After the indentation tests, the Oliver and Pharr method\(^\text{30}\) has been applied to compute the hardness and elastic modulus of the Berkovich indenter. Therefore, Young’s modulus of the rock can be calculated as follows:

\[
E_i = \frac{\sqrt{\pi} S}{2\mu h}\sqrt{\frac{2}{r}}
\]

where \(E_i\) is the reduced modulus, which shows the total deformation of the indenter and the rock, and \(\beta\) is the constant relevant to the geometry of the indenter, which is 1.034 for the Berkovich indenter. Thus, the reduced modulus\(^\text{21}\) can be calculated as follows:

\[
H = \frac{P_{\text{max}}}{A_c}
\]

\[
A_c = 24.56h_c^2
\]

where \(H\) is the hardness, \(P_{\text{max}}\) is the maximum load, \(A_c\) is the contact area, \(h_c\) is the contact depth, and \(\epsilon\) is a constant, which is 0.75 for the Berkovich indenter. Thus, the reduced modulus\(^\text{21}\) can be calculated as follows:

\[
E_i = \frac{\sqrt{\pi} S}{2\mu h}\sqrt{\frac{2}{r}}
\]

where \(E_i\) is the reduced modulus, which shows the total deformation of the indenter and the rock, and \(\beta\) is the constant relevant to the geometry of the indenter, which is 1.034 for the Berkovich indenter. Thus, the reduced modulus\(^\text{21}\) can be calculated as follows:
3. RESULTS

3.1. Mineral Compositions and Organic Matter. The mineral compositions and organic matter (OM) results of the shale samples are shown in Table 1. The dominant mineralogical compositions of the shale samples were quartz and clay. The quartz contents were in the range of 31.5−53.6% with a mean of 42.9%, and the clay contents were in the range of 25.9−45.2% with a mean of 35.0%. The average contents of feldspar, calcite, dolomite, and pyrite were 6.8%, 8.5%, 3.9%, and 2.9%, respectively. The TOC contents of the shale samples were in the range of 1.26−4.18% with a mean of 2.61%. In addition, in this study, EDX analysis was used to acquire more minute information about the mineral compositions of the shale samples, and then, the elemental mapping technique was applied to analyze the shale samples. The existence of silicon and oxygen could be used to determine the location of quartz on the surfaces of the shale samples. The large amount of carbon indicated the presence of OM. K-feldspar could be identified by the presence of potassium, silicon, oxygen, and trace amounts of aluminum. Calcium could be used to identify the presence of calcite. High concentrations of iron and sulfur indicated the presence of pyrite. Finally, the clay- and quartz-rich areas could be recognized using different ratios of aluminum to silicon.

Table 1. Mineral Components and TOC Values of the Longmaxi Formation Shales from the Yibin Area of China

| sample ID no. | quartz (%) | feldspar (%) | calcite (%) | dolomite (%) | pyrite (%) | clay (%) | TOC (%) |
|---------------|------------|--------------|-------------|--------------|------------|---------|---------|
| 1             | 31.5       | 7.6          | 10.2        | 2.7          | 2.8        | 45.2    | 3.34    |
| 2             | 41.3       | 4.8          | 9.5         | 3.4          | 3.5        | 37.5    | 4.18    |
| 3             | 48.8       | 8.9          | 7.4         | 1.8          | 1.6        | 31.5    | 2.35    |
| 4             | 37.2       | 9.5          | 11.6        | 8.7          | 4.2        | 28.8    | 1.26    |
| 5             | 53.6       | 6.4          | 5.8         | 4.7          | 3.6        | 25.9    | 1.73    |
| 6             | 44.9       | 3.6          | 6.3         | 2.2          | 1.8        | 41.2    | 2.88    |

**TOC**, total organic carbon.

3.2. Pore Characteristics of Shales. The FE-SEM images of sample 3 were used to measure the pore characteristics of the Longmaxi Formation shale samples, as shown in Figure 5. Based on the FE-SEM analysis, OM pores, interparticle (interP) pores, and intraparticle (intraP) pores were present in the Longmaxi Formation shales. Most of the OM pores observed in the shale samples exhibited different shapes and sizes (Figure 5a−c). The OM pores between quartzes or carbonates were heterogeneously distributed and had elliptical bubbles and irregular polygon shapes (Figure 5a,b). The OM pores between clay minerals exhibited irregular slit or strip shapes (Figure 5c) because of the effect of the structure of the clay minerals. In particular, some of the clay minerals with mixed OM pores exhibited long strip shapes (Figure 5d). The interP pores in the shale samples were mainly distributed between the quartzes, feldspars, clay minerals, or calcites (Figure 5e−g); they were triangular and polygonal in shape; and were in contact with each other, forming an effective pore network. The sizes of the interP pores were relatively large, ranging from the nanoscale to microracle. The intraP pores were mainly developed within quartzes (Figure 5h) and calcites (Figure 5i), which were relevant to the dissolution in the shales. The intraP pores were relatively small in size and exhibited elliptical or round shapes.

3.3. Load−Displacement Curves. In the experiment, the minerals in the shale samples were divided into two types: soft matters and brittle minerals, mainly including quartz and carbonate particles. Under a light microscope, the brittle minerals were transparent and the soft matters were black, as shown in Figure 6a. The load−displacement curves of the brittle minerals (Figure 6b), the complex minerals at the interfaces (Figure 6c), and the soft matters (Figure 6d) in sample 3 were analyzed using the nanoindentation method, as shown in Figure 7.

Figure 7 illustrates that at the loading stage, two of the load−displacement curves of the brittle minerals were smooth without any abnormal phenomena, while another load−displacement curve of the brittle minerals exhibited some "pop-in" behavior during the loading. This "pop-in" behavior might be caused by the intraP pores in the quartz and carbonates. The recovered elastic deformations of both were large, and the residual deformations of both were small in the unloading stages of all three load−displacement curves. Therefore, it was inferred that the brittle minerals had a dense structure, a high stiffness, and strong mechanical properties. The curves of both the complex minerals and the soft matters exhibited some "pop-in" behaviors during loading. This "pop-in" behavior might be caused by the cracks that formed during the penetrating process when the load reached the yield strength of the shale sample. Another reason for this "pop-in" behavior was that the indenter encountered...
microfractures, interP pores, and soft materials (e.g., clay and kerogen) during loading, and the displacement experienced an abrupt increase. During unloading, the recovered elastic deformations of the soft matters and the complex minerals were small and the residual deformations were large. This demonstrated that the soft matters had a loose and soft structure, a low stiffness, and weak mechanical properties. The residual deformations of the soft matters were the largest, those of the brittle minerals were the smallest, and those of the complex minerals were between those of the brittle minerals and the soft matters. In addition, as shown in the optical micrographs

Figure 4. (a) Raw SEM image of sample 3. (b) EDX mapping of image (a). (c) Element distribution of sample 3.

Figure 5. FE-SEM images of sample 3 from the Longmaxi Formation shales in the Yibin area: OM pores (a–c), the clay minerals with long strip shapes (d), interP pores (e–g), and intraP pores (h,i).
values of the soft matters were as follows: $H$ (0.83 GPa, 0.78 GPa, and 0.94) and $E$ (25.70 GPa, 8.34 GPa, and 0.32). The mechanical test results achieved in this study were basically consistent with the experimental results of other studies. For example, Mavko et al.\textsuperscript{19} confirmed that the elastic modulus of the hard minerals in shales was greater than 70 GPa, Eliyahu et al.\textsuperscript{26} found that the mean value for soft minerals was about 29 GPa, and Shi et al.\textsuperscript{27} confirmed that the elastic modulus of the complex particles at the interfaces was about 59 GPa. The hardness and elastic modulus of brittle minerals were more than 9 times and 3 times those of soft matters, respectively, so the mechanical properties of the two types of minerals were significantly different. The test values of a few soft matters were on the high side because of the strong heterogeneity of the shale samples. In the process of the indenter pressing into the soft matters, the test values became larger because of the contact with brittle minerals or other hard minerals. The mechanical parameters of the same mineral obtained in various tests were different because they were also affected by other factors, including the lattice structure, defects, and impurities, which made accurate measurement very difficult.\textsuperscript{37}

In addition, as shown in Table 2, for the different minerals, the coefficients of variation of the elastic moduli were smaller than those of the hardness values, reflecting an increase in the uncertainties in the property values. The scatter of the hardness was higher than that of the elastic modulus because the contact area was treated as $A_i$ in eq 3. $A_i$ was indefinite because it was calculated using the equation $24.56h_i^2$, which did not consider the roughness and inhomogeneities of the contact surface, which were indefinite quantities.\textsuperscript{34} Compared to the brittle minerals and the complex minerals, the coefficients of variation of the soft matters were the largest. The boxplot function was applied to illustrate the statistical distributions of the hardness and elastic modulus values of the different minerals, as shown in Figure 10. The hardness values exhibited a larger variation because there were outliers that fell outside of the box compared to the elastic modulus values. The change results also had a higher uncertainty because of the uncertain contact area ($A_i$). The brittle minerals had higher hardness and elastic modulus values than other two minerals because of their stable crystalline atomic structures.

3.5. Microdeformation Characteristics of the Shales. Figure 11 shows the deformation characteristics of the three types of minerals in sample 3. The deformation and crack propagation of the three types of minerals were completely different, and their elastic modulus and hardness values were significantly different. The brittle minerals had the largest elastic modulus and hardness values, and the soft matters had the smallest values. The brittle fractures mainly occurred in the surfaces of the brittle minerals. In the process of brittle fracture formation, there was the maximum stress at the point of contact with the edge of the indenter, and the microcracks mainly extended along the edge of the indenter until the minerals completely cracked. However, the growth of the microcracks was affected by the lattice structure of the minerals, resulting in the microcracks that did not necessarily extend along the edge of the indenter.\textsuperscript{36} The plastic deformation mainly occurred in the surface of the soft matters, and the microcracks did not develop significantly around the indentation. The deformation of the complex minerals was between those of the soft matters and the brittle minerals.

The deformation characteristics of the indentation surface were further studied using SEM (Figure 12). Inelastic deformation occurred on the indentation surface of the shale
samples, resulting in the formation of many microcracks, brittle fractures, and plastic deformation features. These results showed that there were few microcracks in the center of the indentation because the microcracks first cracked open and then closed with the intrusion of the indenter (Figure 12a,e). The mineral particles in contact with the edge of the indenter were severely broken as some of the microcracks formed because of the large stress (Figure 12b). In the process of the indenter pressing into the surface of the shale sample, tensile cracks formed around the indentation because of the drag force, and then, they propagated along the edges of the mineral particles (Figure 12c,d,f). To further distinguish between the deformation characteristics of the brittle minerals and the soft matters, energy spectrum analysis (EDS) was applied to measure the mineral compositions of the sample surfaces (Figure 13). The two types of minerals had different deformation characteristics. The brittle minerals, such as quartz (Figure 13a) and carbonate (Figure 13b), were mainly subjected to shear fracturing, while the soft matters mainly underwent plastic deformation and easily formed tensile cracks under the tensile force (Figure 13c). That is, in the process of the indenter pressing into the shale samples, the surface and internal deformation characteristics of the shale became very complex because of the heterogeneity of the mineral distribution. Organic matter, clay, original microcracks, and brittle mineral particles all had an influence on the micromechanical properties of shale samples.39

Figure 8. Statistical distributions of the hardness and elastic modulus values of the (a,b) soft matters, (c,d) complex minerals, and (e,f) brittle minerals in sample 3.

Table 2. Mechanical Parameters of the Different Minerals in Sample 3

| mineral type     | hardness mean (GPa) | hardness standard deviation (GPa) | hardness coefficient of variation | elastic modulus mean (GPa) | elastic modulus standard deviation (GPa) | elastic modulus coefficient of variation |
|------------------|---------------------|-----------------------------------|-----------------------------------|---------------------------|------------------------------------------|-------------------------------------------|
| brittle minerals | 7.65                | 3.34                              | 0.44                              | 85.20                     | 16.10                                     | 0.19                                      |
| complex minerals | 2.69                | 0.90                              | 0.33                              | 56.49                     | 11.76                                     | 0.21                                      |
| soft matters     | 0.83                | 0.78                              | 0.94                              | 25.70                     | 8.34                                      | 0.32                                      |
Figure 9. Histograms of the (a) mean hardness and (b) mean elastic modulus values of the different minerals in sample 3.

Figure 10. Statistical variations in the (a) hardness and (b) elastic modulus values of the different minerals in sample 3.

Figure 11. Optical micrographs of the deformation characteristics of the (a) brittle minerals, (b) complex minerals, and (c) soft matters in sample 3.

Figure 12. SEM images of the indentations on sample 3: few microcracks in the center of the indentation (a,e), severely broken mineral particles in contact with the edge of the indenter (b), and tensile cracks formed around the indentation (c, d, and f).
Figure 13. EDS of the different minerals and SEM images of the indentations (insets): (a) quartz, (b) carbonate, and (c) clay.

Figure 14. Relationships between the elastic modulus and hardness of the (a) soft matters, (b) complex minerals, (c) brittle minerals, and (d) whole shale samples.
4. DISCUSSION

4.1. Relationships between the Mechanical Parameters of the Different Minerals. The relationships between the elastic modulus and hardness values of the soft matters, complex minerals, brittle minerals, and whole shale samples are shown in Figure 14. As shown in Figure 14a–c, the obtained experimental data were scattered, indicating the strong microheterogeneity of the different minerals in the shale samples. The hardness values of a few of the soft matters were relatively large, possibly because the indenter was in contact with brittle minerals or other hard minerals as pressing into the soft matters. The elastic modulus values of the few brittle minerals were relatively small, which might be because of the development of microcracks and micropores in the brittle minerals, such as quartz and carbonate. The elastic modulus and hardness values of the complex minerals were both relatively large because of the existence of brittle or hard minerals. Bao et al. reported that there was a nonlinear relation between the elastic modulus and the hardness of the material, and they provided a nonlinear formula to describe this relationship

\[ E = \sqrt{HR} \tag{8} \]

where \( R \) is the coefficient of the capacity dissipation. In this study, the three minerals had a nonsignificant nonlinear relation between their elastic modulus and hardness values. Through nonlinear fitting with a power function, the correlation coefficients (\( R^2 \)) of the soft matters, complex minerals, and brittle minerals were only 0.474, 0.157, and 0.126, respectively, indicating the weakness of the nonlinear relationship. Therefore, the relation between the elastic modulus and hardness for the whole shale sample was plotted using all of the mechanical parameters of the three minerals (Figure 14d). For the whole shale sample, the elastic modulus increased nonlinearly with increasing hardness, which indicated that the performance of antiplastic deformation increased with the elasticity of the shale sample. By nonlinear fitting, the relation between the elastic modulus and the hardness satisfied a power function with a correlation coefficient of \( R^2 = 0.772 \). Thus, it could be inferred that the local mechanical properties of the shale sample were influenced not only by the mineral components but also by the microcracks and micropores developed in the shale sample, which resulted in a nonlinear relationship between the two mechanical parameters.

4.2. Distribution of the Mechanical Properties at the Nanoscale. At the nanoscale, the mechanical parameters fluctuated because of the heterogeneity of the experimental samples. Therefore, it was necessary to carry out statistical analysis on the nanoindentation results to grasp the uncertainty characteristics. Previous studies had shown that the Weibull model could effectively represent the macroscopic and microscopic heterogeneities of rocks and the mechanical response characteristics of rocks under external environmental conditions. The Weibull model could be expressed as follows:

\[ f(x) = 1 - \exp \left[ -\left( \frac{x - x_0}{X_i} \right)^m \right] \tag{9} \]

where \( f(x) \) is the possibility that the mechanical parameter value is less than \( x \), \( X_i \) is the feature parameter, \( x_0 \) is the minimum variable value (generally set to 0), and \( m \) is the Weibull modulus reflecting the dispersivity of the mechanical parameters. The larger the \( m \) value, the fewer the defects in the test area, and the lower the uncertainty of the parameter. When \( x_0 \) is set to 0, eq 9 can be expressed as follows:

\[ \ln \left[ \ln \left( \frac{1}{1 - f(x)} \right) \right] = m \ln x - m \ln X_i \tag{10} \]

The linear relationship between \( \ln \left[ \ln \left( \frac{1}{1 - f(x)} \right) \right] \) and \( \ln x \) is the key to estimating the Weibull modulus (\( m \)) and the characteristic mechanical parameter (\( X_i \)) using the least-squares method. The steps used to estimate the results of the nanoindentation tests using the least-squares method are as follows. First, the mechanical parameters of \( N \) measuring points were determined, and the hardness and elastic modulus values achieved from the nanoindentation experiments were arrayed in numerical order. Then, the probability of each test result of less than \( x_i \) was calculated using the following equation:

\[ f(x_i) = \frac{i - 0.5}{N} \tag{11} \]

\( N \) pairs of \( (f(x_i), x_i) \) were obtained from eq 11. After that, the linear regression analysis of these \( N \) pairs of \( (f(x_i), x_i) \) was carried out using the least-squares method, and the Weibull distribution moduli of the hardness and elastic modulus values from the nanoindentation tests were computed from the slope and intercept of the plot of \( \ln \left[ \ln \left( \frac{1}{1 - f(x)} \right) \right] \) versus \( \ln x \) (Table 3).

The Weibull distribution curves of the hardness and elastic modulus values from the indentation tests for the soft matters, complex minerals, brittle minerals, and whole shale samples are shown in Figure 15. The results show that all of the \( m \) values of the two mechanical parameters of the soft matters, complex minerals, and brittle minerals were small, indicating a high uncertainty for the results of the nanoindentation tests. The \( m \) values of the hardness were lower than those of the elastic modulus, which indicated that the hardness had a higher uncertainty. The soft matters had the smallest \( m \) value for hardness; this indicates that the calculation of the hardness depended on the projected area of the indentation, but the presence of mineral particles with different strengths caused a phenomenon of clay accumulation in the local area of the indentation, which affected the accuracy of the calculated projection area and thus the precision of the hardness calculated. It could be inferred that a more serious phenomenon of clay accumulation occurred for the soft matters, which also made the hardness values more uncertain. The \( m \) values of the two mechanical parameters of the soft matters were smaller than those of the brittle minerals, indicating that the mechanical parameters of the soft matters had a higher uncertainty too. These results showed that when the indentation fractures propagated into soft matters, the larger and/or stronger mineral particles resulted in greater deflections and obstacles to
the indentation fractures and thus more jumps in the
experimental data. The \( m \) values of the two mechanical
parameters of the complex minerals varied in a complex manner
because of their complex compositions. In addition, for the
whole shale samples, the \( m \) values of the two mechanical
parameters were smaller, which demonstrated that the shale
samples had strong microheterogeneity. It was found that the
\( m \) values for the two mechanical parameters of the whole shale
samples were close to those of the shale samples with vertical
bedding analyzed by Shi et al., in which the \( m \) value of the
elastic modulus was found to be 2.27 and that of the hardness
was found to be 1.01. These facts suggested that the test results
were reliable.

4.3. Effects of the Shale Components on the
Mechanical Properties. When the indenter entered into the
shale sample in the nanoindentation tests, the mechanical
properties of the shale sample were affected by many factors,
such as the clay content, the brittle mineral content, and the
TOC content. Therefore, to determine the relationships
between the mechanical parameter and these influencing factors,
the mechanical parameters of six shale samples with various
mineral compositions were measured using the nanoindentation
tests (Table 4). The plots of the elastic modulus and hardness
versus hard mineral content (siliceous and carbonate minerals
combined), clay content, TOC, and soft component content
(clay and TOC combined) are shown in Figures 16 and 17,
respectively. As shown in Figures 16 and 17, the elastic modulus
and hardness both increased with an increase in hard mineral

![Figure 15. Weibull distribution curves of the hardness and elastic modulus values of the (a,b) soft matters, (c,d) complex minerals, (e,f) brittle
minerals, and (g,h) whole shale samples.](image)

| Table 4. Relationships between the Mineral Compositions
and Mechanical Parameters of the Different Shale Samples |
|---------------------------------------------|
| sample ID No. | quartz + carbonate (%) | clay (%) | TOC (%) | clay + TOC (%) | hardness (GPa) | elastic modulus (GPa) |
|----------------|------------------------|---------|--------|-----------------|----------------|------------------------|
| 1              | 44.4                   | 45.2    | 3.34   | 48.54           | 1.29           | 36.06                  |
| 2              | 54.2                   | 37.5    | 4.18   | 41.68           | 0.47           | 26.67                  |
| 3              | 58.0                   | 31.5    | 2.35   | 33.85           | 2.13           | 42.81                  |
| 4              | 57.5                   | 28.8    | 1.26   | 30.06           | 2.47           | 48.54                  |
| 5              | 64.1                   | 25.9    | 1.73   | 27.63           | 3.27           | 55.72                  |
| 6              | 53.4                   | 41.2    | 2.88   | 44.08           | 1.22           | 40.14                  |

https://doi.org/10.1021/acsomega.1c02049
ACS Omega 2021, 6, 18200–18214

18210
Figure 16. Correlation between the elastic modulus of the shale samples and the (a) quartz + carbonate content, (b) clay content, (c) TOC content, and (d) clay + TOC content.

Figure 17. Correlation between the hardness of the shale samples and the (a) quartz + carbonate content, (b) clay content, (c) TOC content, and (d) clay + TOC content.
contents and decreased with an increase in soft component contents. The elastic modulus exhibited a favorable linear relationship with TOC, particularly when compared with those of the other factors. In this study, it was found that the elastic modulus exhibited a relatively favorable relationship with the TOC content \( R^2 = 0.864 \), while it exhibited relatively weak correlations with the amount of hard minerals \( R^2 = 0.459 \), the clay mineral content \( R^2 = 0.545 \), and the soft component content \( R^2 = 0.614 \). Similarly, the hardness exhibited a relatively favorable linear relationship with the TOC content \( R^2 = 0.824 \), while it exhibited relatively poor relationships with the hard mineral content \( R^2 = 0.506 \), the clay content \( R^2 = 0.662 \), and the soft component content \( R^2 = 0.719 \). To some extent, these correlations illustrated that although the TOC content of the shale sample was less than 5% (seen in Table 4), it had an important effect on the elastic modulus and hardness. The reason for this was that the micro- and nanopores were very well developed because of the high maturity of the shale sample, which decreased the elastic modulus and hardness of the shale sample.\(^{44}\) Therefore, the development degree of the micropores had a significant impact on the micromechanical properties of the shale sample.

5. CONCLUSIONS

In this study, the mineral compositions, organic geochemistry, and pore characteristics of shale samples obtained from the Longmaxi Formation in the Yibin area were characterized using several laboratory techniques. The mechanical properties of the brittle minerals, the soft matters, and the complex minerals at the interfaces in the shale samples were investigated using the nanoindentation method. The Weibull model was used to estimate the uncertainty characteristics of the mechanical parameters of the different minerals. The influences of the microcharacteristics of the shales on the mechanical properties were analyzed for the different shale samples. The following conclusions were drawn.

1. The load–displacement curves of the complex minerals and soft matters exhibited more “pop-in” behaviors than those of the brittle minerals because of the existence of soft materials. The brittle minerals had the largest recovered elastic deformations and the smallest residual deformations, whereas the soft matters had the largest residual deformations and the smallest recovered elastic deformations. Therefore, the brittle minerals were mainly subjected to shear fracturing, whereas the soft matters mainly suffered plastic deformation and easily formed tensile cracks under the tensile force.

2. The brittle minerals had the largest mean hardness and mean elastic modulus values, whereas the soft matters had the smallest mean hardness and mean elastic modulus values. The three types of minerals exhibited non-significant relationships between the elastic modulus and hardness. The coefficients of variation of the hardness were higher than those of the elastic modulus, indicating that the hardness had more scatter due to the uncertain contact area. The Weibull modulus values of the hardness were less than those of the elastic modulus, also confirming that the hardness had a higher uncertainty. The soft matters had the largest coefficients of variation and the smallest Weibull modulus values for the hardness and elastic modulus.

3. For the whole shale sample, the elastic modulus increased nonlinearly with increasing hardness following a power function. The elastic modulus and hardness both exhibited favorable relationships with the TOC content, indicating that the TOC content of the shale samples had an important influence on the elastic modulus and hardness.

■ AUTHOR INFORMATION

Corresponding Author

Yunqian Long — School of Petrochemical Engineering & Environment, Zhejiang Ocean University, Zhoushan, Zhejiang 316022, China; orcid.org/0000-0002-5176-3484; Email: longyunqian@163.com

Authors

Ya Zhang — School of Petrochemical Engineering & Environment, Zhejiang Ocean University, Zhoushan, Zhejiang 316022, China
Xiaohu Huang — School of Petrochemical Engineering & Environment, Zhejiang Ocean University, Zhoushan, Zhejiang 316022, China
Yuyi Wang — School of Petrochemical Engineering & Environment, Zhejiang Ocean University, Zhoushan, Zhejiang 316022, China
Yanhong Zhao — School of Petrochemical Engineering & Environment, Zhejiang Ocean University, Zhoushan, Zhejiang 316022, China
Renyi Wang — School of Petrochemical Engineering & Environment, Zhejiang Ocean University, Zhoushan, Zhejiang 316022, China
Fufuan Song — School of Petrochemical Engineering & Environment, Zhejiang Ocean University, Zhoushan, Zhejiang 316022, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c02049

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was financially supported by the Natural Science Foundation of Zhejiang Province (Project nos. LY19A020004 and LY20D020002), the National Natural Science Foundation of China (Project no. 11602221), the General Research Projects of Zhejiang Provincial Department of Education (Project no. Y201840296), and the Zhoushan Science and Technology Project (Project no. 2019C21028).

■ REFERENCES

(1) Liang, X.; Xu, Z.; Zhang, Z.; Wang, W.; Zhang, J.; Lu, H.; Zhang, L.; Zou, C.; Wang, G.; Mei, J.; Rui, Y. Breakthrough of shallow shale gas exploration in Taiyang anticline area and its significance for resource development in Zhaotong, Yunnan Province, China. Pet. Explor. Dev. 2020, 47, 12–29.
(2) Wang, H.; Ma, F.; Tong, X.; Liu, Z.; Zhang, X.; Wu, Z.; Li, D.; Wang, B.; Xie, Y.; Yang, L. Assessment of global unconventional oil and gas resources. Pet. Explor. Dev. 2016, 43, 925–940.
(3) Ross, D. J. K.; Bustin, R. M. The importance of shale composition and pore structure upon gas storage potential of shale gas reservoirs. Mar. Pet. Geol. 2009, 26, 916–927.
(4) Cho, J.; Kim, H.; Jeon, S.; Min, K. Deformation and strength anisotropy of Asan gneiss, Boryeong shale, and Yeoncheon schist. Int. J. Rock Mech. Min. Sci. 2012, 50, 158–169.

(5) Abushawashi, Y.; Xiao, X.; Astakhov, V. A novel approach for determining material constitutive parameters for a wide range of triaxiality under plane strain loading conditions. Int. J. Mech. Sci. 2013, 74, 133–142.

(6) Liu, Y.; Li, X.; Li, Z.; Chen, P.; Yang, T. Experimental study of the surface potential characteristics of coal containing gas under different loading modes (uniaxial, cyclic and graded). Eng. Geol. 2019, 249, 102–111.

(7) Mansouri, H.; Ajaloeian, R. Mechanical behavior of salt rock under uniaxial compression and creep tests. Int. J. Rock Mech. Min. Sci. 2018, 110, 19–27.

(8) Zhao, J.; Kontsevoi, O. Y.; Xiong, W.; Smith, J. Simulation-aided constitutive law development – Assessment of low triaxiality void nucleation models via extended finite element method. J. Mech. Phys. Solids 2017, 102, 30–45.

(9) Tomičević, Z.; Kodvanj, J.; Hild, F. Characterization of the nonlinear behavior of nodular graphite cast iron via inverse identification—Analysis of uniaxial tests. Eur. J. Mech. A-Solids. 2016, 59, 140–154.

(10) Abedi, S.; Slim, M.; Hofmann, R.; Bryndzia, T.; Ulm, F. J. Nano-chemistry-mechanical signature of organic-rich shales: A coupled indentation—EDX analysis. Acta. Geotech. 2016, 11, 559–572.

(11) 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.

(12) Arson, C.; Pereira, J. M. Influence of damage on pore size distribution and permeability of rocks. Int. J. Numer. Anal. Methods Geomech. 2013, 37, 810–831.

(13) Fauchille, A. L.; Eijnden, A. P.; Ma, L.; Chandler, M.; Taylor, K. G.; Madi, K.; Lee, P. D.; Rutter, E. Variability in spatial distribution of mineral phases in the Lower Bowland Shale, UK, from the mm- to jμm-scale: Quantitative characterization and modelling. Mar. Pet. Geol. 2018, 92, 109–127.

(14) Manjunath, G. L.; Jha, B. Geomechanical characterization of gondwana shale across nano-micro-meso scales. Int. J. Rock Mech. Min. Sci. 2019, 119, 35–45.

(15) Poon, B.; Rittel, D.; Ravichandran, G. An analysis of nanoindentation in linearly elastic solids. Int. J. Solids Struct. 2008, 45, 6018–6033.

(16) Liu, K.; Ostadhassan, M.; Bubach, B. Application of nanoindentation to characterize creep behavior of oil shales. J. Pet. Sci. Eng. 2018, 167, 729–736.

(17) Shi, X.; He, Z.; Long, S.; Peng, Y.; Li, D.; Jiang, S. Loading rate effect on the mechanical behavior of brittle longmaxi shale in nanoindentation. Int. J. Hydrogen Energy 2019, 44, 6481–6490.

(18) Chuang, S.; Lin, S.; Wei, P.; Han, C.; Lin, J.; Chang, H. Characterization of the elastic and viscoelastic properties of dentin by a nanoindentation creep test. J. Biomech. 2015, 48, 2155–2161.

(19) Li, C.; Ostadhassan, M.; Kong, L.; Bubach, B. Multi-scale assessment of mechanical properties of organic-rich shales: A coupled nanoindentation, deconvolution analysis, and homogenization method. J. Pet. Sci. Eng. 2019, 174, 80–91.

(20) Mashhadian, M.; Verde, A.; Sharma, P.; Abedi, S. Assessing mechanical properties of organic matter in shales: Results from coupled nanoindentation/SEM-EDX and micromechanical modeling. J. Pet. Sci. Eng. 2018, 165, 313–324.

(21) Liu, K.; Ostadhassan, M.; Bubach, B. Applications of nanoindentation methods to estimate nanoscale mechanical properties of shale reservoir. J. Nat. Gas. Sci. Eng. 2016, 35, 1310–1319.

(22) Li, C.; Ostadhassan, M.; Guo, S.; Gentzis, T.; Kong, L. Application of PeakForce tapping mode of atomic force microscope to characterize nanomechanical properties of organic matter of the Bakken Shale. Fuel 2018, 233, 894–910.
(43) Abbas, A. K.; Flori, R. E.; Alsaba, M. Estimating rock mechanical properties of the Zubair shale formation using a sonic wireline log and core analysis. J. Nat. Gas. Sci. Eng. 2018, 53, 359–369.

(44) Maruvanchery, V.; Kim, E. Mechanical characterization of thermally treated calcite-cemented sandstone using nanoindentation, scanning electron microscopy and automated mineralogy. Int. J. Rock Mech. Min. Sci. 2020, 125, No. 104158.