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FRACTURE TOUGHNESS ASSESSMENT OF SHALES BY NANOINDENTATION

Yunqui Liu

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FRACTURE TOUGHNESS ASSESSMENT OF SHALES

BY NANOINDENTATION

A Master of Science Project

By

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MASTER OF SCIENCE IN CIVIL ENGINEERING

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Fracture Toughness Assessment of Shales
by Nanoindentation

A Masters Project Presented

by

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ABSTRACT
FRACTURE TOUGHNESS ASSESSMENT OF SHALES
BY NANOINDENTATION

September 2015
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Directed by: Dr. Guoping Zhang

Nanoindentation has been reported as an effective tool for realizing the strength and stiffness (modulus of elasticity) of different materials including thin film materials, cementitious composites and rock or clay mineral materials. However, to the best of the authors’ knowledge, nanoscale fracture of shale materials has rarely been examined. Fracture toughness property of shale has been typically studied by observing crack growth of notched macroscale specimens subjected to flexural or tension loads. This research discusses the possible characterization of fracture toughness of shale using contact mechanics at the nanoscale. The analysis method is based on two traditional fracture toughness measurement methods which are used for some different materials. One is the radial crack length measurement method and the other one is based on evaluating the energy absorbed by radial cracks propagating from the indentation imprint in brittle materials. Nanoindentation experiments performed using Berkovich and Cube corner nanoindenter are reported. The Young’s Modulus, Hardness and fracture toughness of shale are extracted from nanoindentation experiments. Fracture toughness for different types of shale are evaluated using both crack length measurement and an equivalent elastic crack energy approach and are compared to macroscale fracture
toughness of different types of shale from the literature. Mechanical properties for
different types of shale are calculated from nanoindentation tests and mineralogy is found
to play an important role in controlling mechanical properties of shales. An increase in
organic content and clay minerals content decreases both Young’s Modulus and Hardness
of shale. But the deviation of fracture toughness calculation results in this project cannot
be ignored comparing with results from macroscale tests. There is some influence for
fracture toughness measurement by size effect and shale heterogeneity. Shale
heterogeneity and compositional variability should be considered as serious challenges in
quantifying the mechanical properties of shale in the future work.
TABLE OF CONTENTS

ACKNOWLEDGMENTS ........................................................................................................ III

ABSTRACT ........................................................................................................................ IV

TABLE OF CONTENTS ....................................................................................................... VI

LIST OF TABLES ................................................................................................................ IX

LIST OF FIGURES ............................................................................................................. X

LIST OF SYMBOLS ........................................................................................................ XIII

LIST OF ABBREVIATIONS .............................................................................................. XIV

1 INTRODUCTION ........................................................................................................ 1
   1.0 General .................................................................................................................. 1
   1.1 Indentation-based methods to assess fracture toughness ...................................... 1
   1.2 Objectives of Research ......................................................................................... 2
   1.3 Scope of Research .................................................................................................. 3
   1.4 Organization of Thesis .......................................................................................... 3

2 LITERATURE REVIEW .............................................................................................. 4
   2.0 Introduction ........................................................................................................... 4
   2.1 Nano Mechanical Characterization of Shale ....................................................... 5
   2.2 Measurement of Fracture Toughness by Nanoindentation Methods .................. 5

3 Character and property of different types of Shale .................................................. 7
   3.0 Introduction .......................................................................................................... 7
   3.1 Opalinus Clay Shale .............................................................................................. 7
   3.2 Antrim Shale ......................................................................................................... 7
   3.3 Utica Shale ............................................................................................................ 8

4 Mechanical Testing by Instrumented Indentation .................................................... 10
   4.0 Introduction .......................................................................................................... 10
4.1 Indentation Modulus ................................................................. 11
4.2 Hardness ........................................................................................ 12
4.3 Different Indenters Used in testing .............................................. 13
  4.3.1 Berkovich Indenter Tip .............................................................. 13
  4.3.2 Cube Corner Indenter Tip ............................................................ 14
  4.3.3 The Differences between Berkovich Indenter Tip and Cube Corner
      Indenter Tip ..................................................................................... 15
4.4 Continuous Stiffness Measurement ............................................. 16
5 EXPERIMENTAL PROGRAM ......................................................... 17
  5.0 Introduction .................................................................................. 17
  5.1 Specimen Preparation ................................................................. 17
  5.2 Specimen Testing .......................................................................... 20
    5.2.1 Antrim Shale ........................................................................... 20
    5.2.2 Opalinus Clay Shale ................................................................. 22
    5.2.3 Utica Shale ............................................................................ 24
    5.2.4 Comparison mechanical properties results of different types of shale ..... 26
  5.3 Different Measurements of Fracture Toughness ......................... 28
    5.3.1 Introduction .......................................................................... 28
    5.3.2 Crack Length Measurement Method .................................... 28
    5.3.3 Energy Method ..................................................................... 29
  5.4 Characterization of Microstructure ............................................. 32
6 FRACTURE TOUGHNESS MEASUREMENT ANALYSIS ............... 33
  6.0 Introduction .................................................................................. 33
  6.1 Materials and Methods .............................................................. 33
  6.2 Antrim Shale ............................................................................. 34
6.2.1 Crack length measurement............................................................................ 34
6.2.2 Energy Approach............................................................................................ 38
6.3 Opalinus Clay Shale with bedding direction surface......................................... 44
   6.3.1 Crack length measurement............................................................................ 44
   6.3.2 Energy Approach............................................................................................ 52
6.4 Opalinus Clay Shale with normal to bedding direction surface....................... 55
7 SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS......................... 59
   7.1 Summary........................................................................................................... 59
      7.1.1 Antrim Shale ............................................................................................. 59
      7.1.2 Opalinus Clay Shale .................................................................................. 59
   7.2 Conclusions....................................................................................................... 61
   7.3 Recommendations............................................................................................. 62
REFERENCES.......................................................................................................... 63
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 4-1  Summary of shape properties of Berkovich and Cube-corner indenter tips</td>
<td>15</td>
</tr>
<tr>
<td>Table 5-1  Summary of sand paper information</td>
<td>18</td>
</tr>
<tr>
<td>Table 6-1  Summary of crack length measurement analysis results (Antrim Shale)</td>
<td>37</td>
</tr>
<tr>
<td>Table 6-2  Summary of energy approach measurement analysis results (Antrim Shale)</td>
<td>43</td>
</tr>
<tr>
<td>Table 6-3  Summary of crack length measurement analysis results (Opalinus Clay Shale)</td>
<td>51</td>
</tr>
<tr>
<td>Table 6-4  Summary of energy approach measurement analysis results (Opalinus Clay Shale with bedding direction)</td>
<td>54</td>
</tr>
<tr>
<td>Table 6-5  Summary of energy approach measurement analysis results for Opalinus Clay Shale with normal to bedding direction surface</td>
<td>58</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 4.1</td>
<td>Basic theory of load displacement process for nanoindentation</td>
<td>11</td>
</tr>
<tr>
<td>Figure 5.1</td>
<td>Polishing Machine</td>
<td>18</td>
</tr>
<tr>
<td>Figure 5.2</td>
<td>Sand paper with different grade</td>
<td>19</td>
</tr>
<tr>
<td>Figure 5.3</td>
<td>Alumina Lapping Film with different grade</td>
<td>19</td>
</tr>
<tr>
<td>Figure 5.4</td>
<td>Different types of Shale Samples after Polishing</td>
<td>20</td>
</tr>
<tr>
<td>Figure 5.5</td>
<td>Load-displacement curves of Antrim Shale from nanoindentation</td>
<td>21</td>
</tr>
<tr>
<td>Figure 5.6</td>
<td>Average Young’s Modulus-displacement analysis of Antrim Shale from nanoindentation</td>
<td>21</td>
</tr>
<tr>
<td>Figure 5.7</td>
<td>Average Hardness-displacement analysis of Antrim Shale from nanoindentation</td>
<td>22</td>
</tr>
<tr>
<td>Figure 5.8</td>
<td>Load-displacement curves of Opalinus Clay Shale from nanoindentation</td>
<td>23</td>
</tr>
<tr>
<td>Figure 5.9</td>
<td>Average Young’s Modulus-displacement analysis of Opalinus Clay Shale from nanoindentation</td>
<td>23</td>
</tr>
<tr>
<td>Figure 5.10</td>
<td>Average Hardness-displacement analysis of Opalinus Clay Shale from nanoindentation</td>
<td>24</td>
</tr>
<tr>
<td>Figure 5.11</td>
<td>Load-displacement curves of Utica Shale from nanoindentation</td>
<td>25</td>
</tr>
<tr>
<td>Figure 5.12</td>
<td>Average Young’s Modulus-displacement analysis of Utica Shale from nanoindentation</td>
<td>25</td>
</tr>
<tr>
<td>Figure 5.13</td>
<td>Average Hardness-displacement analysis of Utica Shale from nanoindentation</td>
<td>26</td>
</tr>
<tr>
<td>Figure 5.14</td>
<td>Comparison of Utica shale and Antrim shale by organic content</td>
<td>27</td>
</tr>
<tr>
<td>Figure 5.15</td>
<td>Comparison of Utica shale and Opalinus Clay shale by clay mineral content</td>
<td>28</td>
</tr>
<tr>
<td>Figure 5.16</td>
<td>Schematic illustration of cube corner indentation</td>
<td>29</td>
</tr>
<tr>
<td>Figure 5.17</td>
<td>Schematic of a load-displacement curve, showing a step during the loading cycle and associated energy release</td>
<td>30</td>
</tr>
<tr>
<td>Figure 5.18</td>
<td>SEM Image of Opalinus Clay Shale with bedding direction surface</td>
<td>32</td>
</tr>
</tbody>
</table>
Figure 5.19  SEM Image of Opalinus Clay Shale with normal to bedding direction surface........................................................................................................................................ 32

Figure 6.1  Indentation after testing with 4000nm displacement control ......................... 34
Figure 6.2  Indentation after testing with 6000nm displacement control ......................... 34
Figure 6.3  Indentation after testing with 8000nm displacement control ......................... 35
Figure 6.4  Highlighted cracks of indentation with 4000nm displacement control........... 35
Figure 6.5  Highlighted cracks of indentation with 6000nm displacement control........... 35
Figure 6.6  Highlighted cracks of indentation with 8000nm displacement control........... 35
Figure 6.7  Load-displacement curve with 4000nm displacement control....................... 38
Figure 6.8  Load-displacement curve with 6000nm displacement control....................... 39
Figure 6.9  Load-displacement curve with 8000nm displacement control....................... 39
Figure 6.10 Analysis image with 4000nm displacement control.................................... 40
Figure 6.11 Analysis image with 6000nm displacement control.................................... 41
Figure 6.12 Analysis image with 8000nm displacement control.................................... 41
Figure 6.13 SEM image of indentations on Opalinus clay shale surface ........................ 44
Figure 6.14 #1 indentation SEM image........................................................................... 45
Figure 6.15 #3 indentation SEM image........................................................................... 45
Figure 6.16 #4 indentation SEM image........................................................................... 46
Figure 6.17 #5 indentation SEM image........................................................................... 46
Figure 6.18 #6 indentation SEM image........................................................................... 47
Figure 6.19 #7 indentation SEM image........................................................................... 47
Figure 6.20 #8 indentation SEM image........................................................................... 48
Figure 6.21 #9 indentation SEM image........................................................................... 48
Figure 6.22 #11 indentation SEM image.......................................................................... 49
Figure 6.23 #6 indentation with highlight defined cracks............................................. 49
Figure 6.24 #9 indentation with highlight defined cracks............................................. 50
Figure 6.25 #11 indentation with highlight defined cracks............................................. 50
Figure 6.26 Typical load-displacement curve for nanoindentation of Opalinus Clay Shale .......................................................... 52
Figure 6.27 Typical analysis image for energy approach of Opalinus Clay Shale........... 53
Figure 6.28  Typical SEM image of indentation of Opalinus Clay Shale with normal to bedding direction surface ................................................................. 55
Figure 6.29  Typical load-displacement curve for Opalinus Clay Shale with normal to bedding direction surface ................................................................. 56
Figure 6.30  Typical analysis image of energy approach for Opalinus Clay Shale with normal to bedding direction surface ................................................................. 56
# LIST OF SYMBOLS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Units</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>GPa</td>
<td>Young’s Modulus</td>
</tr>
<tr>
<td>H</td>
<td>GPa</td>
<td>Hardness</td>
</tr>
<tr>
<td>$E_r$</td>
<td>GPa</td>
<td>Reduced Modulus</td>
</tr>
<tr>
<td>$h_c$</td>
<td>nm</td>
<td>Contact depth</td>
</tr>
<tr>
<td>$A_c$</td>
<td>nm</td>
<td>Contact area</td>
</tr>
<tr>
<td>S</td>
<td>mN/nm</td>
<td>Stiffness</td>
</tr>
<tr>
<td>$U_t$</td>
<td>J</td>
<td>Total energy</td>
</tr>
<tr>
<td>$U_e$</td>
<td>J</td>
<td>Elastic energy</td>
</tr>
<tr>
<td>$U_p$</td>
<td>J</td>
<td>Plastic energy</td>
</tr>
<tr>
<td>$U_{pp}$</td>
<td>J</td>
<td>Pure plastic energy</td>
</tr>
<tr>
<td>$U_{frac}$</td>
<td>J</td>
<td>Fracture energy</td>
</tr>
<tr>
<td>P</td>
<td>mN</td>
<td>Load</td>
</tr>
<tr>
<td>$c$</td>
<td>μm</td>
<td>Radial crack length</td>
</tr>
<tr>
<td>$K_{1c}$</td>
<td>$MPa\sqrt{m}$</td>
<td>Fracture stress intensity factor</td>
</tr>
<tr>
<td>$C_{ave}$</td>
<td>μm</td>
<td>Average radial crack length</td>
</tr>
</tbody>
</table>
# LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOC</td>
<td>Total organic carbon</td>
</tr>
<tr>
<td>SRM</td>
<td>Standard reference material</td>
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<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>CSM</td>
<td>Continuous stiffness measurement</td>
</tr>
</tbody>
</table>
1 INTRODUCTION

1.0 General

Shale is a fine-grained rock often composed of clay and other minerals. The predominance of clays influences its mechanical properties and typically imparts a strong elastic anisotropy. Shales are often rich in organic material called kerogen which acts as a source during hydrocarbon generation. Shale formations are interesting to the oil and gas industry because they host vast natural gas and oil resources. Gas flows to the wellbore primarily through natural and induced fractures. The natural fractures are caused by tectonic forces, desiccation and hydrocarbon generation while the process of hydraulic fracturing stimulates and induces fractures.

Advances in drilling technology have increased profitability of shale gas. Thus, the ability to form extensive, stable fractures in the shale is directly related to the profitability of gas production from shales.

Mechanical properties especially the fracture toughness property is necessary in the design of these fractures; however, because of the mineralogical variability of shale, mechanical properties vary considerably. Many shales are chemically and mechanically unstable making recovery of suitably sized samples for standard mechanical testing impossible. Nano-indentation testing of drilling cuttings provides a viable and economically attractive option for recovering needed mechanical properties. Thus, the purpose of this project was to use instrumented indentation testing to measure the mechanical properties and then use different fracture toughness measurements to calculate the $K_{IC}$ values for different types of shale.

1.1 Indentation-based methods to assess fracture toughness

The ability of a material to resist cracking, or fracture, has been vital to the studies of fracture mechanics. It is challenging to accurately determine the fracture toughness of brittle materials due to the difficulty in creating sharp pre-cracks without catastrophically failing the specimen. The study of fracture toughness is usually analyzed at a macro range using high load to create a large indent with long cracks at the edge. However, this
technique is limited when the test samples are used in a delicate environment or have special structures such as thin films and micro features. The capability of making accurate and repeatable measurements in a localized area at small loads makes nanoindentation system an ideal tool for fracture toughness study on small samples.

In this project, the fracture toughness of different types of shale was calculated using different experienced equation. The traditional evaluation method was used by direct measurements of radial cracks created with a sharp diamond indenter. However, most clay shale samples could not present radial crack on the sample surfaces. Energy release and energy approach methods which were used in hydrated cement paste were considered for fracture toughness measurement for shale.

1.2 Objectives of Research

As mentioned earlier, Instrumented Indentation method has been used in mechanical testing of Shale in some study. Based on the former research, nanoindentation can be used to evaluate the fracture toughness of materials and interfaces in a similar manner to that conventionally used in larger scale testing. The traditional method is used to calculate the fracture toughness using elastic modulus, hardness, load-displacement process and radial crack lengths measured on the sample surface after indentation.

The objectives of the research are:

1. To develop polishing methods for different types of shale with different surface conditions.
2. To develop nanoindentation testing program with Berkovich and Cube-corner tips measuring the properties of shale.
3. To compare former methods used to measure fracture toughness of different materials and develop more effective analysis method for fracture toughness analysis of different types of shale.
4. To analyze fracture toughness analysis results and SEM images of shale sample surfaces after indentation, evaluate the process and method used for this research.
1.3 Scope of Research

The research utilized G200 Nanoindentation system to measure the elastic modulus and hardness of shale samples, and analyze fracture toughness determinations using traditional radial crack length measurement and energy approach methods. The scope of the research involved designing shale samples for nanoindentation tests and different methods to analyze the fracture toughness of different types of shale.

1.4 Organization of Thesis

Chapter 2 presents a background review of relevant literature pertaining to the justification of this research and several different methods used for fracture toughness analysis. It includes information on Opalinus Clay Shale, Antrim Shale, Utica Shale, and an introduction into other techniques in nanoindentation.

Chapter 3 presents the character and properties of different types of shale including Opalinus Clay Shale, Antrim Shale and Utica Shale based on the experienced tests and information presented in the literature.

Chapter 4 presents the characterization and technique information of nanoindentation system and an introduction of continuous stiffness measurement technique using in this research.

Chapter 5 presents the experimental program followed in this study. It includes information on the materials used, preliminary lab work, experimental setup, and methods testing/analysis.

Chapter 6 presents the experimental analysis of fracture toughness analysis of different types of shale using different methods including traditional radial crack analysis method and energy approach analysis method. Image analysis method is also used in this part to calculate the amount of energy during loading and unloading process.

Chapter 7 presents the overall conclusions based on the results and recommendations for future work.
2 LITERATURE REVIEW

2.0 Introduction

Fracture toughness of different types of shale were studied in this project based on the former research and literature about mechanical property measurement using nanoindentation and different fracture toughness measurement methods developed by other scientists.

The increase in price of conventional oil and decline in petroleum reserves make shale reservoirs an attractive alternative source of hydrocarbon fuel (Esene et al., 2007). The development of shale gas is made possible by horizontal drilling and multistage mechanical properties of shales have been poorly sampled primarily because of their chemical and mechanical instability. It is difficult to recover suitable samples of shale for conventional mechanical property measurements especially fracture toughness measurements. Organic rich and clay minerals rich shale are intrinsically heterogeneous and complex. Organic content present in shales can either act as an effective source or a potential source (Jarvie, 1991). Shale heterogeneity and compositional variability present serious challenges in quantifying the mechanical properties of shale. These can only be overcome with adequate statistical sampling. Nano-indentation technology can eliminate the need of larger samples thus allow improved statistical sampling.

Fracture toughness measurements using nanoindentation technique have been developed for several years to calculate different type materials. Because there has also been a growing interest in identifying fracture toughness parameters of different materials using nanoindentation (Scholz et al. 2004). To the best of the authors’ knowledge, such analysis has not been applied to shale material yet. The major challenge in determining fracture toughness of materials using nanoindentation is the difficulty to obtain robust measurement of submicron crack propagation as the stress increases. There have been some suggestions of post measurement of the crack length extended from the edge of the indentation impression after unloading. This measurement can be determined using optical microscopes or atomic force microscope. Such measurements have been shown
possible with metallic and thin film specimens (Li et al. 1997). However, there is considerable difficulty to obtain these measurements from shale material with the multiple cracking in the shale. Moreover, stable propagation of radial cracks, or what is known as picture-frame cracks, under nanoindentation load has been questioned by many researchers (Chen & Bull 2007) and is a function of the material examined. A robust method for determining fracture toughness from nanoindentation can be based on energy assumptions independent of measuring radial crack propagation.

2.1 Nano Mechanical Characterization of Shale

Because of the mineralogical variability of shale, mechanical properties vary considerably. Many shales are chemically and mechanically unstable making recovery of suitably sized samples for standard mechanical testing impossible. Hay et al. (2010) used nanoindentation testing of drill cuttings, fragments or sidewall cores provides a viable and economically attractive option for recovering needed mechanical properties in order to use instrumented indentation testing high-load option measure the mechanical properties of small volumes of Barnett shale. Kumar et al. (2012) reported on nanoindentation study of shales from the Barnett, Woodford, Ordovician, Eagle Ford and Haynesville plays. They used careful selection of load and displacement during nanoindentation testing to yield mechanical properties, such as Young’s Modulus and Hardness.

2.2 Measurement of Fracture Toughness by Nanoindentation Methods

The study of fracture toughness is usually analyzed at a macro range using high loads to create a large indent with long cracks at the edge. However, this technique is limited when the test samples are used in a delicate environment or have special structures. The capability of making accurate and repeated measurements in localized areas at small loads makes nanoindentation system an ideal tool for fracture toughness study on small samples. Another reason using nanoindentation to determine the mechanical property especially the fracture toughness property is the difficulty and expensive to get core samples for macroscale fracture testing.

Based on the radial crack length measurement method, Palmqvist noted that the crack length varied as a linear function of the indentation load. Lawn, Evans, and
Marshall formulated a different relationship, where they treated the fully formed radial crack and found the ration $P/c^{3/2}$ is a constant, the value of which depends on the specimen material.

Another fracture toughness measurement method used in this project is based on the energy analysis, which has been developed by some material researchers. For instance, Rosenfeld et al. (1990) developed an analytical model to determine the mixed mode interfacial fracture toughness of epoxy coatings on soda-lime glass substrates using micro-indentation. The method is based on computing the strain energy consumed in annular plate located above the crack using mechanics of materials. The elastic energy release rate can then be calculated by differentiating the energy with respect to the crack area. Field et al. (2003) computed the fracture toughness based on pop-in penetration. Pop-in occurs due to change in crack morphology when the median crack nucleates and propagates upward at the boundary of plastic zone to join the existing radial cracks. This results in extra penetration at the same indentation load level. The pop-in effect becomes negligible in materials whose microstructures contain a distribution of voids in various sizes because the pop-in effect due to these voids would dominate. Chen & Bull (2007) studied the fracture in thin optical coating on glass. Experiments on glass showed that well-developed radial cracks might not be observed when indenting thin films. This is contrary to the case of indenting a bulk material where radial cracks are well-developed and in some cases measureable. Therefore, an energy approach to estimate the fracture toughness was proposed. The proposed approach takes into account the effect of through thickness fracture. The total energy during indentation can be decomposed to elastic, plastic, fracture and other negligible energies. The total and elastic energies can be computed from the nanoindentation load-penetration curve. The plastic energy can be computed as the difference between the elastic and total energy. Cheng et al. (2002) suggested computing the plastic energy as a function of the residual to total penetration ratio.
3 Character and property of different types of Shale

3.0 Introduction

In this project, there are three different types of shale were used for fracture toughness measurement analysis. In order to analyze the influence of organic and clay minerals content for the mechanical characterization of shale, the shale samples which were used in this project have different organic and clay minerals content. The reference properties are recommended by former researches using macro-scale test.

The obvious difference of organic and clay minerals content is the motivation to use these three types of shale. The Opalinus Clay Shale contains more clay minerals than Utica Shale, as well the Antrim Shale includes more organic minerals than Utica Shale.

3.1 Opalinus Clay Shale

Opalinus Clay Shale samples are collected from the study site known as the Mont Terri rock laboratory (Canton Jura, Switzerland), which is operated by an international consortium including several organizations dealing with radioactive waste disposal. The Opalinus Clay Shale is located at a depth of about 270m below the surface. It shows strong alignment of illite-smectite, kaolinite, chlorite, and calcite.

The mineralogical composition of the Opalinus Clay Shale includes 40-70 wt.% clay minerals, 10-30 wt.% carbonates (mainly calcite, subordinate siderite, and ankerite), 10-30 wt.% quartz and accessory feldspars, pyrite, and organic matter.

3.2 Antrim Shale

The Antrim Shale is a formation of Upper Devonian age in the Michigan Basin, in the US state of Michigan, and extending into Ohio and Indiana. It is a major source of natural gas in the northern part of the basin. The Antrim Shale was defined by A. C. Lane in 1901, and named for type-section exposures in Antrim County, Michigan. The formation was previously known as the St. Cleric Shale in Michigan, and the Genessee Shale in Indiana.
The Antrim is a brown to black, pyritic, highly laminated and organic-rich shale, from 60 to 220 feet thick. Total organic content varies from 1% to 20%. In some places the unit includes a gray calcareous shale or limestone, and in places a fine-grained sandstone at the base.

The formation is called the Kettle Point Formation in Ontario, and is the stratigraphic equivalent of the New Albany Shale in the Illinois Basin. It is overlain by the Bedford Shale, and underlain in some areas by the Jordan River Formation, and elsewhere by the Thunder Bay Limestone.

The Antrim Shale, is a major source of shale gas, and produces natural gas along a swath across the northern part of the state. Most natural gas production is in Antrim, Crawford, Montmorency, Oscoda and Otsego counties.

3.3 Utica Shale

The Utica Shale is a stratigraphical unit of Middle Ordovician age in the Appalachian Basin. It underlies much of the northeastern United States and adjacent parts of Canada. It takes the name from the city of Utica, New York, as it was first described as an outcrop along the Starch Factory Creek east of the city by Ebenezer Emmons in 1842.

The Utica Shale is calcareous and organic-rich shale. It is a major source of tight gas in Quebec, and is rapidly becoming so in Ohio.

The Utica Shale lies under most of New York, Pennsylvania, Ohio, and West Virginia and extends under adjacent parts of Ontario and Quebec in Canada and Kentucky, Maryland, Tennessee, and Virginia in the United States. Parts of the island of Montreal consist of Utica shale, which affected construction of parts of the Montreal metro. In some regions of Pennsylvania, the Utica Shale reaches to almost two miles below water level. However, the depth of the Utica Shale rock decreases to the west into Ohio and to the northwest towards Canada. It reaches a thickness of up to 1,000 feet (300 m) and can be as thin as 70 feet (20 m) towards the margins of the basin. 250 feet (80 m) are exposed in the type section.
Based on the research of mineralogical and TOC trends in the Ohio Utica Shale, [Harrington et al., 2013] average total organic carbon across all samples is about 1.70%. And the average weight of clay minerals is from 37% to 45%, the carbonates are from 19% to 44%.
4 Mechanical Testing by Instrumented Indentation

4.0 Introduction

Indentation testing is a simple method that consists essentially of touching the material of interest whose mechanical properties such as elastic modulus and hardness are unknown with another material whose properties are known. Nanoindentation techniques initially evolved as a tool used in mechanical characterization of materials at small scale. Originally, this method was applied to homogeneous materials such as metals, alloys and ceramics which can be modeled as continuous elastic half space (Oliver & Pharr, 1992, 2004). However, this technique has evolved as a versatile tool; methods have evolved to extend its uses with different shapes of indenter. So has its application beyond continuum materials; to thin films, polymers, biological specimens and geo-materials.

Nanoindentation is technique whereby an indenter tip of known geometry and mechanical properties is used to make an impression in a sample, with a penetration depth and force dynamically measured at resolutions of nanometers and micronewtons respectively. The resulting force-depth curve can be analyzed to give bulk properties such as modulus and hardness, as well as to study deformation mechanisms. Oliver and Pharr method (Oliver and Pharr, 2002) which is the extension of Doerner and Nix (1986) method is frequently used to determine indentation modulus and hardness. During loading deformation is modeled as both elastic and plastic, however, unloading is assumed to be pure elastic recovery (Oliver and Pharr, 2002). Corresponding load-displacement is presented in Figure 4.1. Next few sections are devoted to derivations of mechanical properties using indentation curves.
4.1 Indentation Modulus

Indentation modulus is derived as

\[
E_r = \frac{\sqrt{\pi}}{2\beta \sqrt{A_c}} S
\]

\[
S = \frac{dP}{dh} h_{max}
\]
Where $\beta$ is dimensionless correction factor for indenter tip shape and $\beta=1.05$ is commonly used for Berkovich indenter (Oliver and Pharr 2004). $A_c$ is the projected contact area between indenter and sample, which can be obtained solely using indentation parameters (Oliver & Pharr, 1992, 2004; Sneddon, 1965).

$$A_c = C_0 h_c^2 + \sum_{j=1}^{8} C_j h_c^{(3j)/2}$$

where contact depth $h_c$ is defined as

$$h_c = h - \frac{F}{S}$$

where $\varepsilon$ is a constant that depends on indenter tip and used 0.75 for Berkovich indenter. For perfect Berkovich indenter lead term $C_0$ is 24.5 and $C_j$ ($j=1, 2, \ldots, 8$) are needed to describe the deviations of the Berkovich tip shape to inevitable rounding effect at the tip due to manufacturing artifacts.

The relation between the reduced and elastic modulus of the sample and indenter is expressed as (Doerner & Nix, 1986)

$$\frac{1}{E_r} = \frac{1-v^2}{E} + \frac{1-\nu_i^2}{E_i}$$

where $v$ and $\nu_i$ are the Poisson’s ratio of the sample and indenter, and $E$ and $E_i$ are the Young’s modulus of the indenter and sample respectively. Previous studies suggest that the Poisson’s ratio of the tested material has no significant influence on the Young’s modulus (Mencik et al., 1997) a constant $\nu = 0.25$ is assumed for mica samples. For a diamond indenter, $E_i = 1141$ GPa and $\nu_i = 0.07$ (Oliver & Pharr, 1992).

For axisymmetric indenter and isotropic material, indentation modulus is independent of tip geometry (Pharr et al., 1992) and given as

$$E_r = \frac{E}{1-v^2}$$

### 4.2 Hardness

Indentation hardness, $H$, is simply the measure of mean indentation stress at maximum load and given as
where $F_{\text{max}}$ is the maximum force and $A_c$ is the contact area given by equations introduced before for $F_{\text{max}}$. These equations indicate that indentation modulus and hardness are not independent parameters and related by

$$E_r \propto \sqrt{H}$$

### 4.3 Different Indenters Used in testing

#### 4.3.1 Berkovich Indenter Tip

The Berkovich indenter tip is the most frequently used indenter tip for instrumented indentation testing to measure mechanical properties on the nanoscale. The Berkovich indenter tip is a three-sided pyramid that can be ground to a point and thus maintains a self-similar geometry to very small scales. It is ideal for most testing purposed. It is not easily damaged and can be readily manufactured. It includes plasticity at very small loads which produces a meaningful measure of hardness.

The Berkovich indenter tip has a large included angle of 142.3° which minimizes the influence of friction. The Berkovich indenter tip is available as a traceable standard.

The mean contact pressure is usually determined from a measure of the contact depth of penetration, $h_c$, such that the projected area of the contact is given by:

$$A = 3\sqrt{3} h_c^2 \tan^2 \theta$$

Which for $\theta=65.27^\circ$, evaluates to:

$$A = 24.494 h_c^2$$

$$\approx 24.5 h_c^2$$

and hence the mean contact pressure, or hardness, is:
Since it is customary to use the mean contact pressure as a definition of hardness in nanoindentation, Berkovich indenters used in nanoindentation work are designed to have the same ratio of projects area to indentation depth as the Vickers indenter in which case the face angle is 65.27°. The equivalent cone angle is 70.296°. From geometry, the ratio of the length of one side of the residual impression is related to the total depth of penetration by a factor of about 7.5. And the representative strain within the specimen material is approximately 8%.

4.3.2 Cube Corner Indenter Tip

The Cube Corner indenter tip is a three-sided pyramid with mutually perpendicular faces arranged in geometry like the corner of a cube. The centerline-to-face angle for this indenter is 34.3° whereas for the Berkovich indenter it is 65.3°. The sharpness of the cube corner indenter tip produces much higher stresses and strain in the area of the contact. This is useful in producing very small, well-defined cracks around hardness impressions in brittle materials. These cracks can be used to estimate fracture toughness at very small scales. It is available as a traceable standard.

Despite the acuteness of the indenter, it is still possible to perform nanoindentation testing in the normal manner and the expression for the projected area of contact:

\[
A = 3\sqrt{3} h_c^2 \tan^2 \theta
\]

\[
= 2.60 h_c^2
\]

The equivalent cone angle for a cube corner indenter evaluates to 42.278°. The ratio of the length of a side of the residual impression to the total penetration depth is approximately 2.6. That is, the size of the impression on the surface is about 2.6 times as large as the total penetration depth.
### 4.3.3 The Differences between Berkovich Indenter Tip and Cube Corner Indenter Tip

The summary of both the Berkovich indenter tip and cube corner indenter tip property is presented in the Table 4-1 Summary of shape properties of Berkovich and Cube-corner indenter tips

<table>
<thead>
<tr>
<th></th>
<th>Berkovich</th>
<th>Cube-Corner</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Shape</strong></td>
<td>3-sided pyramid</td>
<td>3-sided pyramid w/perpendicular faces</td>
</tr>
<tr>
<td><strong>Centerline-to-face angle</strong></td>
<td>65.3°</td>
<td>35.2644°</td>
</tr>
<tr>
<td><strong>Area (projected)</strong></td>
<td>24.56d²</td>
<td>2.5981d²</td>
</tr>
<tr>
<td><strong>Volume-depth relation</strong></td>
<td>8.1873d³</td>
<td>0.8657d³</td>
</tr>
<tr>
<td><strong>Projected area/face area</strong></td>
<td>0.908</td>
<td>0.5774</td>
</tr>
<tr>
<td><strong>Equivalent cone angle</strong></td>
<td>70.32°</td>
<td>42.28°</td>
</tr>
</tbody>
</table>

As mentioned before, the Berkovich indenter has a relatively large face angles, which ensures that deformation is more likely to be described by the expanding cavity model rather than slip-line theory, which is equivalent to saying that the stresses beneath the indenter are very strongly compressive. In some instances, it is desirable to indent a specimen with more of a cutting action, especially when intentional radial and median cracks are required to measure fracture toughness. A cube corner indenter offers a relatively acute face angle that can be beneficial in these circumstances.
4.4 Continuous Stiffness Measurement

Nanoindentation is now commonly used for the study of mechanical properties of materials on the nanoscale because of the ease and speed with which it can be carried out. One of the significant improvements in nanoindentation testing is the continuous stiffness measurement (CSM) technique. It offers a direct measure of dynamic contact stiffness during the loading portion of an indentation test and, being somewhat insensitive to thermal drift, allows an accurate observation of small volume deformation.

The CSM is accomplished by imposing a small, varying signal on top of a DC signal that drives the motion of the indenter. By analyzing the response of the system by means of a frequency specific amplifier data are obtained. This allows the measurement of contact stiffness at any point along the loading curve and not just at the point of unloading as in the conventional measurement. The CSM technique makes the continuous measurement of mechanical properties of materials possible in one sample experiment without the need for discrete unloading cycles, and with a time constant that is at least three orders of magnitude smaller than the time constant of the more conventional method of determining stiffness from the slope of an unloading curve. The measurements can be made at exceedingly small penetration depths. Thus, this technique is ideal for mechanical property measurements of nanometer thick films. Furthermore, its small time constant makes it especially useful for measuring the properties of polymeric materials. In nonuniform materials, such as graded materials and multilayers, the microstructure and mechanical properties change with indentation depth. Continuous measurements of mechanical properties of these materials during indentation are greatly needed.
5 EXPERIMENTAL PROGRAM

5.0 Introduction

This chapter presents the experimental program used for this project. For the samples used for nanoindentation, sample preparation is an essential requirement especially for shale samples what have much different mineral content. The equipment and materials used for polishing were introduced in this chapter.

The mechanical properties such as Young’s Modulus and Hardness were calculated using nanoindentation program. The average values of those mechanical properties for each sample had been calculated using analysis software of nanoindentation.

In order to analyze the fracture toughness properties of different types of shale, both of the radial crack length measurement and energy method had been used in this project. And the microstructure of Opalinus Clay Shale was analyzed using SEM images.

5.1 Specimen Preparation

Sample preparation is an important step to ensure quality results from Nanoindentation tests. ASTM Standard E2546, applied for nano-indentation testing states that “the surface finish of the sample will directly affect the test results. The test should be performed on a suitably prepared surface” (ASTM, 2007).

Smoothness of sample surface is important because contact area is calculated from the contact depth and area function assuming surface before indentation is perfectly smooth. Furthermore, if the indenter encounters a rough surface it will glance off the ridges yielding inaccurate readings. The degree of mechanical polishing of any material is associated with its heterogeneity. On the microscale, shale is composed of several minerals, some hard like, quartz, intermediate like calcite, and soft like clay and kerogen. This mineralogic heterogeneity in shale leads to difficulty in polishing. Harder phases can be polished easily whereas softer phases tend to have scratches or are pulled out even
after fine polishing. The inability to obtain a perfectly smooth surface leads to large standard deviations in the calculated modulus.

In this project, mechanically polishing using sand paper of different grit size with gradual transition from 800 to 4000 is used as the first step. (See Table 5-1) The polishing equipment and sand paper are shown in the Figure 5.1 and Figure 5.2. While polishing, the top and bottom surfaces of samples were ensured to be perfectly parallel. After attaining sufficient smoothness, different grades Alumina Lapping Films were used for final polishing. The grades are from 3 micron to 0.3 micron with different colors. (Figure 5.3)

![Figure 5.1 Polishing Machine](image)

<table>
<thead>
<tr>
<th>Grit Size</th>
<th>Approx. Micron Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>400[P800]</td>
<td>22</td>
</tr>
<tr>
<td>600[P1200]</td>
<td>15</td>
</tr>
<tr>
<td>1200[P2500] MicroCut S Disc</td>
<td>8</td>
</tr>
<tr>
<td>P4000 MicroCut S Disc</td>
<td>5</td>
</tr>
</tbody>
</table>
For each shale sample, because of the influence of the surface direction, there are two perpendicular orientations have been polished for test. One of them is the direction parallel to the bedding direction of the sample, the other one is the direction perpendicular to the bedding direction. Samples were glued on the disks which were used as sample holder for the nanoindentation test. The samples after polishing are presented in Figure 5.4.
5.2 Specimen Testing

5.2.1 Antrim Shale

Nanoindentation CSM Module was used to measure the mechanical properties of Antrim shale. The 2000 displacement control method was used for 22 individual tests.

From the Figure 5.5, the maximum load is about 40 mN, and curves for each individual test have similar trend. From the Figure 5.6 and Figure 5.7, the average value of Young’s Modulus is 8.6 GPa and the average value of Hardness is 0.45 GPa, which were used for fracture toughness calculation in the next chapter.
Figure 5.5 Load-displacement curves of Antrim Shale from nanoindentation

Figure 5.6 Average Young’s Modulus-displacement analysis of Antrim Shale from nanoindentation
5.2.2 Opalinus Clay Shale

Nanoindentation CSM Module was used to measure the mechanical properties of Opalinus Clay Shale. The 3000 displacement control method was used for 11 individual tests.

From the Figure 5.8, the maximum load is about 50 mN, and curves for each individual test have similar trend except some individual test curves had pop-ins on the loading part because of the delamination on the sample surface during loading. From the Figure 5.9 and Figure 5.10, the average value of Young’s Modulus is about 30 GPa a little higher than the results got from Berkovich indenter tip and the average value of Hardness is about 2 GPa, which were used for fracture toughness calculation in the next chapter.
Figure 5.8 Load-displacement curves of Opalinus Clay Shale from nanoindentation

Figure 5.9 Average Young’s Modulus-displacement analysis of Opalinus Clay Shale from nanoindentation
5.2.3 Utica Shale

Nanoindentation CSM Module was used to measure the mechanical properties of Utica shale. The 2000 displacement control method was used for 12 individual tests and some of them had been ignored because of the incorrect data could not be used for analysis.

From the Figure 5.11, the maximum load is about 400 mN, and curves for each individual test have similar trend except some individual test curves had pop-ins on the loading part because of the delamination on the sample surface during loading. From the Figure 5.12 and Figure 5.13, the average value of Young’s Modulus is about 60 GPa and the average value of Hardness is about 8 to 9 GPa.
Figure 5.11 Load-displacement curves of Utica Shale from nanoindentation

Figure 5.12 Average Young’s Modulus-displacement analysis of Utica Shale from nanoindentation
5.2.4 Comparison mechanical properties results of different types of shale

Based on research, the differences of mineral content of shale could affect the mechanical properties of different types of shale. Clay minerals content and organic carbon content, which were two main difference of mineral content in the shales used for this project, were compared to present the influence of them for different types of shale rock.

Figure 5.14 presented the comparison of Utica shale and Antrim shale by organic content. Because the organic content of Utica shale is 1.5% which is much lower than that of Antrim shale, both Young’s Modulus and Hardness of Utica shale are bigger than those of Antrim shale. The increase of organic content in shale decreases both Young’s Modulus and Hardness.
Figure 5.15 presented the comparison of Utica shale and Opalinus Clay shale by clay minerals content. Because the clay minerals content of Utica shale is less than 40% which is lower than that of Opalinus Clay shale, both Young’s Modulus and Hardness of Utica shale are bigger than those of Opalinus Clay shale. The increase of clay minerals content in shale decreases both Young’s Modulus and Hardness of shale.
5.3 Different Measurements of Fracture Toughness

5.3.1 Introduction
The study of fracture toughness is usually analyzed at a macro range using high loads to create a large indent with long cracks at the edge. However, this method is limited when the test samples have special structures such as thin films and micro features. The capability of making accurate and repeatable measurements in localized areas at small loads makes nanoindentation an ideal tool for fracture toughness study on small samples.

The radial crack length measurement and energy approach measurement were used to calculate the fracture toughness property in this project.

5.3.2 Crack Length Measurement Method
Fracture toughness evaluates the ability of a material containing a crack to resist brittle fracture. It can be assessed using indentation technique by making direct measurement of cracks created with a sharp diamond indenter. A relationship exists

![Figure 5.15 Comparison of Utica shale and Opalinus Clay shale by clay mineral content](image)
between the fracture toughness, $K_c$, and the average crack length from the center of the indent to the tips of the cracks, $c$, of the form:

$$K_c = \alpha \left( \frac{E}{H} \right)^{1/2} \left( \frac{P}{c^2} \right)$$

where $P$ is the applied indentation load, and $\alpha$ is an empirical constant which depends on the indenter geometry. For the cube corner indenter $\alpha=0.032$, while for the Vickers and Berkovich indenters $\alpha=0.016$. Therefore, the cube corner indenter is usually selected as it can significantly reduce the cracking thresholds.

![Figure 5.16 Schematic illustration of cube corner indentation](image)

### 5.3.3 Energy Method

There are two different energy methods, one is used to calculate the energy release when there is delamination on the sample and the other one is used for quasi-brittle material without pop-ins on the load-displacement curves.

Li et al. (1999) developed the energy release measurement method for thin films material. The fracture toughness is calculated with the analysis of the energy release in cracking. As they established in their previous work, fracture process progresses in three stages: (1) first ring-like through-thickness cracks form around the indenter by high stresses in the contact area, (2) delamination and buckling occur around contact area at the film interface by high lateral pressure, (3) second ring-like through-thickness cracks and spalling are generated by high bending stresses at the edges of the buckled film. In the Figure 5.17, the energy difference before and after the crack generation is the area of
ABC, i.e., this energy stored in ABC will be released as strain energy to create the ring-like through-thickness crack. According to the theoretical analysis, the fracture toughness of thin films can be written as

\[ K_{IC} = \left[ \frac{E}{(1 - \nu^2)2\pi C_R} \left( \frac{U}{t} \right) \right]^{1/2} \]

where \( E \) is the elastic modulus, \( \nu \) is the Poisson’s ratio, \( 2\pi C_R \) is the crack length in the film plane, \( U \) is the strain energy difference before and after cracking, and \( t \) is the film thickness.

![Figure 5.17 Schematic of a load-displacement curve, showing a step during the loading cycle and associated energy release](image)

The analysis method is based on the energy approach originally introduced for ductile materials by Cheng et al. (2002). It is assumed that the fracture energy is accounted for as a portion of the irreversible energy can be defined as the sum of the energy due to pure plasticity and the energy due to the extension of cracking, describe as

\[ U_{ir} = U_{pp} + U_{crack} \]

The energy due to pure plasticity can be computed from the ratio of plastic to total energy after Cheng et al. (2002)
\[
\frac{U_{pp}}{U_t} = 1 - \left[ \frac{1 - 3 \left( \frac{h_f}{h_m} \right)^2 + 2 \left( \frac{h_f}{h_m} \right)^3}{1 - \left( \frac{h_f}{h_m} \right)^2} \right]
\]

where \( h_f \) is the residual indentation depth, \( h_m \) is the maximum indentation depth, and \( U_t \) is the total energy obtained from fitting a power law function to the loading portion of the indentation curve and substituting into the equation

\[ U_e = \int_{h_r}^{h_{MAX}} P_{UL} dh \]

The pure plastic energy can be found by multiplying the right hand side of the portion equation by the total energy. Once the plastic energy is determined, the cracking energy can be determined from the equation

\[ U_{crack} = U_{ir..U_{pp}} \]

The critical energy release rate \( G_c \) can then be determined as

\[ G_c = \frac{\partial U_{fra}}{\partial A} = \frac{U_{fra}}{A_m} \]

where \( A \) is the contact area given for the cube corner indenter tip used for nanoindentation tests based on the maximum contact depth by substituting \( h_{max} \) into equation

\[ A = 2.6h^2 + 125.6h \]

This theory assumes that the crack growth under nanoindentation load is stable. The fracture stress intensity factor \( K_c \) can be computed from the energy release rate and reduced modulus as

\[ K_{1c} = \sqrt{G_cE_r} \]
5.4 Characterization of Microstructure

In order to analyze the influence of mineral for different types of shale, SEM was used for the Opalinus clay Shale. There are two different directions were captured images for this clay shale. One orientation is the bedding direction, and the other orientation is the direction perpendicular to the bedding direction.

The Figure 5.18 and Figure 5.19 presented the microstructure of Opalinus clay shale. It indicated that the Opalinus clay shale contained a large percent of clay minerals from Figure 5.19.

Figure 5.18  SEM Image of Opalinus Clay Shale with bedding direction surface

Figure 5.19  SEM Image of Opalinus Clay Shale with normal to bedding direction surface
6 FRACTURE TOUGHNESS MEASUREMENT ANALYSIS

6.0 Introduction

Fracture toughness measurement analysis for Antrim shale and Opalinus clay shale is based on the results from nanoindentation testing. The load-displacement curves were presented with the load-displacement data point for each individual test, whereas the average value of Young’s Modulus and Hardness were calculated using Analyze Nanoindentation program. Microscope and SEM images were used to measure the radial crack length for each indentation, image analysis software was used to measure the accurate values for each individual test. Then the equations used for the cement and other materials were used to calculate the fracture toughness of Antrim shale and Opalinus clay shale. There is a deviation range for each group of tests, the average values for each group of tests are shown in the analysis part.

The crack length measurement method and energy approach method have been used to calculate the fracture toughness for both Antrim and Opalinus clay shale with the test results using nanoindentation. Microscope on the Nanoindentation G200 system and JEOL JCM-5000 NeoScope scanning electron microscope were used to capture the image of each individual indentation. Image analysis software was used to measure three different orientation crack length for each indentation. Comparison of $K_{IC}$ values from different measurement methods was presented in the summary. The calculation procedures for each method of different shales are summarized in several tables.

6.1 Materials and Methods

Antrim shale and Opalinus clay shale were used for the fracture toughness analysis, which contain obvious different clay minerals and organic. The average organic content of Antrim shale is about 20% according to some former research, the Young’s Modulus and Hardness are smaller than those of other shale materials which have less organic content. On the other hand, the Opalinus clay shale contains more clay mineral which is about 70 weight percent. While both of the Young’s Modulus and Hardness is smaller than those of other shale materials which have less clay minerals.
Both of the crack length measurement and energy approach have been used to measure the fracture toughness for these shales. For the Antrim shale, the microscope images for each indentation test were captured with the nanoindentation G200 program directly, then the three different orientation crack length were measured using image analysis software. The results based on the energy approach were calculated with the load-displacement curves for both of the Antrim shale and Opalinus clay shale. For the Opalinus clay shale, SEM images for each indentation test were captured with the JEOL JCM-5000 NeoScope scanning electron microscope, then three different orientation crack length were measured using image analysis software.

6.2 Antrim Shale

6.2.1 Crack length measurement

In order to produce obvious cracks on the sample surface for the measurement, three different displacement control programs were developed to test the Antrim shale. The different displacements are 4000nm, 6000nm, 8000nm, which are made as parameters for CSM mode of nanoindentation testing. The images of each test are shown in Figure 6.1, Figure 6.2 and Figure 6.3.

![Indentation after testing with 4000nm displacement control](Image)

**Figure 6.1** Indentation after testing with 4000nm displacement control

![Indentation after testing with 6000nm displacement control](Image)

**Figure 6.2** Indentation after testing with 6000nm displacement control
With the images for each indentation, image analysis software was used to highlight the cracks and measure the length for every crack on the images. The indentation images with highlighted cracks are presented in Figure 6.4, Figure 6.5 and Figure 6.6.
The summary of calculation results using crack length measurement method is presented in the Table 6-1.
Table 6-1  Summary of crack length measurement analysis results (Antrim Shale)

<table>
<thead>
<tr>
<th>Test #</th>
<th>α</th>
<th>E (GPa)</th>
<th>H (GPa)</th>
<th>P (mN)</th>
<th>c1</th>
<th>c2</th>
<th>c3</th>
<th>c_ave(μm)</th>
<th>c_ave(m)</th>
<th>Kc (MPa√m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4000nm 04</td>
<td>0.032</td>
<td>8.86</td>
<td>0.45</td>
<td>21.4</td>
<td>9.88</td>
<td>9.76</td>
<td>7.64</td>
<td>9.09</td>
<td>9.0933E-06</td>
<td>0.111</td>
</tr>
<tr>
<td>6000nm 02</td>
<td>0.032</td>
<td>8.86</td>
<td>0.45</td>
<td>46.3</td>
<td>14.55</td>
<td>17.83</td>
<td>15.77</td>
<td>16.05</td>
<td>0.00001605</td>
<td>0.102</td>
</tr>
<tr>
<td>6000nm 03</td>
<td>0.032</td>
<td>8.86</td>
<td>0.45</td>
<td>45.8</td>
<td>15.62</td>
<td>13.65</td>
<td>15.93</td>
<td>15.07</td>
<td>1.5067E-05</td>
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</tr>
<tr>
<td>6000nm 04</td>
<td>0.032</td>
<td>8.86</td>
<td>0.45</td>
<td>46.6</td>
<td>24.82</td>
<td>20.41</td>
<td>23.82</td>
<td>23.02</td>
<td>2.3017E-05</td>
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</tr>
<tr>
<td>8000nm 01</td>
<td>0.032</td>
<td>8.86</td>
<td>0.45</td>
<td>53.3</td>
<td>26.67</td>
<td>25.57</td>
<td>26.27</td>
<td>26.17</td>
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<td>0.057</td>
</tr>
<tr>
<td>8000nm 02</td>
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<td>8.86</td>
<td>0.45</td>
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<td>28.82</td>
<td>28.17</td>
<td>27.36</td>
<td>28.12</td>
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<tr>
<td>8000nm 03</td>
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<td>8.86</td>
<td>0.45</td>
<td>57.6</td>
<td>31.33</td>
<td>31.27</td>
<td>59.14</td>
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<tr>
<td>8000nm 04</td>
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<td>0.45</td>
<td>57.0</td>
<td>32.99</td>
<td>32.64</td>
<td>52.57</td>
<td>39.40</td>
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<td>0.033</td>
</tr>
</tbody>
</table>
6.2.2 Energy Approach

The analysis method is based on the energy approach originally introduced for ductile materials by Cheng et al. (2002). It is assumed that the fracture energy is accounted for as a portion of the irreversible energy, rather than total energy. The irreversible energy can be defined as the sum of the energy due to pure plasticity and the energy due to the extension of cracking.

The total energy, elastic energy, residual depth and maximum indentation depth can be calculated from the load-displacement curves, the typical load-displacement curves for different displacement control are presented in the Figure 6.7, Figure 6.8 and Figure 6.9.

![Figure 6.7 Load-displacement curve with 4000nm displacement control](image-url)
Figure 6.8  Load-displacement curve with 6000nm displacement control

Figure 6.9  Load-displacement curve with 8000nm displacement control
Then, image analysis software was used to define the area of total energy and the elastic energy. Typical analysis images are presented in the Figure 6.10, Figure 6.11 and Figure 6.12.

Figure 6.10 Analysis image with 4000nm displacement control
Figure 6.11 Analysis image with 6000nm displacement control

Figure 6.12 Analysis image with 8000nm displacement control
In these analysis images, two different colors were used to define the area of different energy. The red area was defined as the irreversible energy producing with loading, whereas the blue area was defined as the elastic energy which was recovered after unloading. The summation of blue and red area is total energy for each indentation test.

The residual indentation and maximum indentation depth can also be calculated directly from the load-displacement curves, the summary of fracture toughness results using energy approach is presented in Table 6-2.
Table 6-2  Summary of energy approach measurement analysis results (Antrim Shale)

<table>
<thead>
<tr>
<th>Test #</th>
<th>hm (nm)</th>
<th>hf (nm)</th>
<th>hf/h</th>
<th>Er (GPa)</th>
<th>Ut (mN*nm)</th>
<th>Upp/Ut</th>
<th>Upp (mN*nm)</th>
<th>Ue (mN*nm)</th>
<th>Ucrack (mN*nm)</th>
<th>Uf (mN*nm)</th>
<th>Kc (MPa*√m)</th>
<th>hm (m)</th>
<th>Am (m2)</th>
<th>Gc (Nm/m2)</th>
<th>Ke (MPa/m)</th>
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<tbody>
<tr>
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<td>4379</td>
<td>3832</td>
<td>0.8</td>
<td>9.53</td>
<td>33971.74</td>
<td>0.82</td>
<td>27747.75</td>
<td>5584.81</td>
<td>639.18</td>
<td>6.39179E-10</td>
<td>0.00000</td>
<td>4379</td>
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</tr>
<tr>
<td>4000nm 03</td>
<td>4373</td>
<td>3835</td>
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<td>9.53</td>
<td>32676.97</td>
<td>0.82</td>
<td>26778.47</td>
<td>5262.47</td>
<td>636.03</td>
<td>6.36035E-10</td>
<td>0.00000</td>
<td>4373</td>
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<td>0.35</td>
</tr>
<tr>
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<td>9.53</td>
<td>34129.38</td>
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<td>680.16</td>
<td>6.80155E-10</td>
<td>0.00000</td>
<td>4379</td>
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<td>69850.02</td>
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<td>5625</td>
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<td>9.53</td>
<td>101459.88</td>
<td>0.79</td>
<td>80549.55</td>
<td>18004.05</td>
<td>2906.28</td>
<td>2.90628E-09</td>
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<td>26.1</td>
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<td>5277.61</td>
<td>5.27761E-09</td>
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<td>101662.18</td>
<td>37197.76</td>
<td>11458.28</td>
<td>1.14583E-08</td>
<td>0.00000</td>
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<td>82234.33</td>
<td>29836.14</td>
<td>9446.19</td>
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<td>130816.31</td>
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<td>108477.56</td>
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<td>8705</td>
<td>1.9702E-10</td>
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</table>
6.3 Opalinus Clay Shale with bedding direction surface

6.3.1 Crack length measurement

Because the Opalinus clay shale is a kind of clay-rich shale, the delamination and bucking of overlapping clay mineral were produced during the loading process. Based on the initial tests, the cracks on the sample surface were difficult to define using microscope. In order to capture obvious indentations image and measure the length of cracks, SEM was used for the Opalinus clay shale analysis. The image of the group indentations used for fracture toughness analysis is presented in Figure 6.13.

![SEM image of indentations on Opalinus clay shale surface](image)

Figure 6.13  SEM image of indentations on Opalinus clay shale surface

Most of obvious indentations were used to measure the length of cracks individually. The images of each indentation with smaller scale are shown from Figure 6.14 to Figure 6.22.
Figure 6.14  #1 indentation SEM image

Figure 6.15  #3 indentation SEM image
Figure 6.16  #4 indentation SEM image

Figure 6.17  #5 indentation SEM image
Figure 6.18 #6 indentation SEM image

Figure 6.19 #7 indentation SEM image
Figure 6.20  #8 indentation SEM image

Figure 6.21  #9 indentation SEM image
Crack length for each indentation was measured on the SEM images directly. Because of the delamination around the initial indentations, personal judgment was applied for some measurement. Some typical images with highlight cracks are shown from Figure 6.23 to Figure 6.25.
The summary of crack length analysis results is presented in Table 6-3.
Table 6-3  Summary of crack length measurement analysis results (Opalinus Clay Shale)

<table>
<thead>
<tr>
<th>Test #</th>
<th>α</th>
<th>E  (GPa)</th>
<th>H  (GPa)</th>
<th>P  (mN)</th>
<th>c1</th>
<th>c2</th>
<th>c3</th>
<th>c\text{ave}(\mu\text{m})</th>
<th>c\text{ave}(\text{m})</th>
<th>K_c  (MPa√m)</th>
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<tbody>
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<td>1.57</td>
<td>34.50</td>
<td>5.50</td>
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<td>4.36</td>
<td>6.58</td>
<td>5.12</td>
<td>0.00000512</td>
<td>0.372</td>
</tr>
</tbody>
</table>
6.3.2 Energy Approach

The analysis method is based on the energy approach originally introduced for ductile materials by Cheng et al. (2002). It is assumed that the fracture energy is accounted for as a portion of the irreversible energy, rather than total energy. The irreversible energy can be defined as the sum of the energy due to pure plasticity and the energy due to the extension of cracking.

The total energy, elastic energy, residual depth and maximum indentation depth can be calculated from the load-displacement curves, a typical load-displacement curve is shown in the Figure 6.26.

![Typical load-displacement curve for nanoindentation of Opalinus Clay Shale](image)

Figure 6.26 Typical load-displacement curve for nanoindentation of Opalinus Clay Shale

The energy analysis with image analysis is as same as the method used for Antrim shale. The image analysis software was used for calculating the area with loading and unloading processes. Some essential parameter can be calculated from the load-displacement curves, a typical analysis image is presented in the Figure 6.27.
In the analysis images, two different colors were used to define the area of different energy. The red area was defined as the irreversible energy producing with loading, whereas the blue area was defined as the elastic energy which was recovered after unloading. The summation of blue and red area is total energy for each indentation test.

The residual indentation and maximum indentation depth can also be calculated directly from the load-displacement curves, the summary of fracture toughness results using energy approach measurement is presented in Table 6-4.
Table 6-4  Summary of energy approach measurement analysis results (Opalinus Clay Shale with bedding direction)

<table>
<thead>
<tr>
<th>Test #</th>
<th>hm (nm)</th>
<th>hf (nm)</th>
<th>hf/ hm</th>
<th>Er (GPa)</th>
<th>Ut (mN*n m)</th>
<th>Upp/Ut</th>
<th>Upp (mN*nm)</th>
<th>Ue (mN*n m)</th>
<th>Ucrack (mN*nm)</th>
<th>Ufra (N*m)</th>
<th>hm (m)</th>
<th>Am (m2)</th>
<th>Gc (Nm/m 2)</th>
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</table>
6.4 Opalinus Clay Shale with normal to bedding direction surface

Based on the mechanical properties from nanoindentation testing, both of the Young’s Modulus and Hardness of samples with normal to bedding direction surface are smaller than those of samples with bedding orientation surface. In order to compare the different of fracture toughness property between different surface orientations, the energy approach measurement was used to calculate the fracture toughness property of Opalinus clay shale with sample surface which is perpendicular to the bedding direction.

Because of the unobvious cracks on the sample surface captured using SEM, the crack length measurement was difficult to use to calculate the fracture toughness property of Opalinus clay shale with normal to bedding direction surface. A typical SEM image is presented in the Figure 6.28.

![Typical SEM image of indentation of Opalinus Clay Shale with normal to bedding direction surface](image)

Figure 6.28 Typical SEM image of indentation of Opalinus Clay Shale with normal to bedding direction surface

As same as the energy approach measurement used for the other surface orientation sample, the parameters used to calculate the fracture toughness can be calculated with load-displacement curves for each individual test, such as total energy, elastic energy, residual depth and maximum depth. These parameters can be read directly
from the load-displacement curves or calculated using image analysis as the other surface orientation sample. A typical load-displacement curve of Opalinus clay shale with normal to bedding direction surface is presented in the Figure 6.29.

![Figure 6.29](image)

**Figure 6.29** Typical load-displacement curve for Opalinus Clay Shale with normal to bedding direction surface

Image analysis software was also used for each individual load-displacement of this sample, a typical analysis image is shown in the Figure 6.30.

![Figure 6.30](image)

**Figure 6.30** Typical analysis image of energy approach for Opalinus Clay Shale with normal to bedding direction surface
With the total energy, elastic energy, residual depth and maximum depth, the pure plastic energy can be calculated with the nominal equation. Then, the fracture energy, maximum contact area and reduced Modulus can be combined to calculate the fracture toughness result. The summary of energy approach measurement results for Opalinus clay shale with normal to bedding direction surface is presented in the Table 6-5.
Table 6-5  Summary of energy approach measurement analysis results for Opalinus Clay Shale with normal to bedding direction surface

<table>
<thead>
<tr>
<th>Test #</th>
<th>hm (nm)</th>
<th>hf (nm)</th>
<th>hf/ hm</th>
<th>Er (GPa)</th>
<th>Ut (mN*n m)</th>
<th>Upp /Ut</th>
<th>Upp (mN*nm)</th>
<th>Ue (mN*n m)</th>
<th>Ucrack (mN*nm)</th>
<th>Ufra (N*m)</th>
<th>hm (m)</th>
<th>Am (m2)</th>
<th>Gc (Nm/m 2)</th>
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7 SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

7.1 Summary

In order to analyze the fracture toughness property of different types of shale, nanoindentation was used to measure the mechanical properties and produce obvious crack for the shale samples. Based on the research, crack length measurement method and energy approach measurement were used for fracture toughness analysis. The comparisons of results using different measurement method are presented in the discussion chapter for both of the organic shale and clay shale.

7.1.1 Antrim Shale

The two proposed method were able to extract the fracture toughness of Antrim shale which is organic rich shale. Comparing the observed results to macroscale observations might provide some insight on the scale effect. Experiments by Kim and Nubeen (1980) on Antrim shale showed fracture toughness of Antrim shale ranges between 1.02-1.18 MPa$\sqrt{m}$ which is bigger than the range of fracture toughness values calculated from the nanoindentation experiments using both of the crack length measurement and energy approach measurement. The average value using crack length measurement is $0.07 \pm 0.04$ MPa$\sqrt{m}$, while the average value using energy approach measurement is $0.52 \pm 0.18$ MPa$\sqrt{m}$.

The Antrim shale samples used for nanoindentation test were rock chips, which were very different from the core samples used for macroscale fracture toughness measurement. As Antrim shale is a kind of brittle material, the mechanical properties may change during ageing time. However, the influence of the indenter tip shape and the roughness of sample surface are other reasons for the high standard deviation in the results.

7.1.2 Opalinus Clay Shale

The two proposed methods were able to extract the fracture toughness of Opalinus clay shale with bedding direction surface which is clay rich shale. But for the Opalinus
clay shale with normal to bedding direction surface, there is no obvious cracks produced on the sample surface using. The crack length measurement method was only used for the Opalinus clay shale with bedding direction surface.

Comparing the observed results to macroscale observations might provide some insight on the scale effect. Experiments by Mont Terri Project (2009) on Opalinus clay shale showed fracture toughness of Opalinus clay shale with bedding direction is $0.53 \pm 0.09\ MPa\sqrt{m}$, while fracture toughness of Opalinus clay shale with normal to bedding direction is $0.12 \pm 0.03\ MPa\sqrt{m}$, which are smaller than the average value ranges of fracture toughness values calculated from the nanoindentation experiments using energy approach measurement. But the experiment’s result is similar with the value calculated using crack length measurement method. For the Opalinus clay shale with bedding direction, the average value using crack length measurement is $0.40 \pm 0.12\ MPa\sqrt{m}$, while the average value using energy approach measurement is $1.23 \pm 0.32\ MPa\sqrt{m}$. For the Opalinus clay shale with normal to bedding direction, the average value using energy approach measurement is $0.88 \pm 0.28\ MPa\sqrt{m}$.

While the fracture toughness values extracted using nanoindentation analysis reasonably compare to values from the literature, a wide scatter in the fracture characteristics extracted from nanoindentation can be observed. This scatter is represented by the relatively high standard deviation and can be attributed to the limited number of indentations reported.

It also should be note that for a quasi-brittle material such as Opalinus clay shale a single radial crack as in metals or organic-rich shale would not develop. Instead many nano-cracks would develop in the fracture process zone. Therefore, the proposed method assumes an equivalent elastic radial crack to simulate the energy consumed in the fracture process zone. This assumption is in line with quasi-brittle fracture mechanics assumptions suggested by some researchers. The effect of any inelasticity is assumed negligible.
7.2 Conclusions

Fracture toughness parameters of Antrim shale and Opalinus clay shale with different surface orientation were determined using nanoindentation. The fracture toughness measurements were calculated using both of the crack length measurement method and energy approach measurement. The crack length measurement method is based on measuring the crack length directly using microscale images and calculating with the mechanical properties by nanoindentation. The energy approach measurement is based on decomposing the plastic energy to pure plastic energy used in producing the irreversible indentation and cracking energy that helps crack propagation. An equivalent elastic radial crack is assumed and the energy required to extend this crack is computed. The cracking energy is computed using the experimentally observed nanoindentation loading and unloading curves. The energy approach method avoids the need to measure radial cracks which proved difficult with clay mineral layers. The fracture toughness parameters were found to have some differences with macroscale fracture toughness of shale for both of the Antrim shale and Opalinus clay shale reported in the literature.

Comparison of the fracture toughness parameters with crack length measurement method and energy approach, the values with crack length measurement were smaller than the other ones. And there was a range of standard deviation for the fracture toughness parameters using different measurement methods.

Based on the mechanical properties especially the fracture toughness property calculated using nanoindentation, size effect for nanoindentation need to be considered in the analysis. However, the influence of mineral heterogeneity of shale is another reason for the deviation of testing results.

Comparison of mechanical properties of different shales with different content of organic and clay mineral indicated that the increases in organic or clay mineral content decrease the Young’s Modulus and Hardness of shale.
7.3 Recommendations

Based on the analysis of mechanical properties from nanoindentation, the roughness of sample affected the results. Because sample preparation is an important step to ensure quality results from nanoindentation results, some other polishing methods for shale sample preparation could be used in the future work. For example, lapping film with smaller grades could be more useful for final polishing. After attaining sufficient smoothness, broad beam argon ion milling could be used for final polishing except the disadvantage of high temperature in the equipment.

In order to measure the crack length using microscope or SEM images, some better equipment could be used to capture more obvious images. And without coating for the shale sample prepared for SEM test, the sample surface should be less disturbed.

In this project, CSM Module of nanoindentation was used to run the tests for each shale sample. On the other hand, DCM Module could be used to do the tests with smaller load and High-load Module could be used to do the tests with deeper displacement or higher load to be suitable for different shale sample testing requirement.

There are two different shales were used to measure the fracture toughness, while another shale was tested for comparison. Even though Antrim shale is organic-rich shale, and Opalinus clay shale is clay–rich shale, more different types of shale with different mineral content should be tested to analyze the influence of different mineral content.

Because of the roughness of sample surface was not good enough to run large number tests directly, some group tests with about ten indentations were done in this project. After better final polishing, hundreds of indentation tests could be done on each sample, and the average value of Young’s Modulus and Hardness should be more accurate.
REFERENCES


