ABSTRACT: Hydrocarbon production from unconventional resources especially shale reservoirs has tremendously increased during the past decade. Eagle Ford shale formation is one of the major sources of oil and gas in United States. However, due to extremely low permeability of this formation, stimulation treatments are implemented for hydrocarbon production. Eagle Ford shale requires a very high breakdown pressure during fracturing treatment due to high mechanical strength and low permeability. This study aims to address these challenges through applying the acidizing treatment on the shale and studying its impact. A detailed experimental investigation was carried out in this work to evaluate mechanical integrity and mineralogical and morphological changes of the shale formation when exposed to HCl acidizing treatment. Two crucial aspects of acidizing treatment, that is, impact of acid concentrations and treatment time, were given additional focus in this study. Different parameters such as porosity, nanopermeability, uniaxial compressive strength (UCS), acoustic velocities, dynamic elastic parameters, rock surface hardness (RSH) and brittleness index (BI) were analyzed before and after the acidizing treatment for different HCl concentrations. Microimaging was done through scanning electron microscopy (SEM) and whole cores were scanned using medical computed tomography (MCT) to understand the small-scale features. X-ray diffraction was used for the minerals’ identification. A continuous profile of UCS was measured through the scratch test system. Post-treatment results revealed that HCl treatment has a profound impact on rock mechanical properties of Eagle Ford shale. Considerable mass loss in core plugs was recorded after treatment at each concentration. Mineralogical composition and microimaging revealed compositional changes and porosity enhancement after the treatment. Reaction rate is higher in the first 10 min for higher acid concentrations resulting in significant changes in properties in that time interval. UCS and RSH exhibited a progressive decrease with increasing concentrations. The rate of RSH reduction increased with the increase in acid concentrations nonlinearly. Acoustic velocities exhibited a considerable decrease even at low acid concentrations due to the enhancement of pore spaces. Noticeable reduction was observed in dynamic rock stiffness and BI with the increase in acid concentrations. On the contrary, Poisson’s ratio showed a significant increment. Experimental findings of this research can be used to optimize the acidizing treatment for Eagle Ford shale and other similar formations. Formation breakdown pressure can be reduced significantly by applying the acid treatment to improve the production of hydrocarbons. Furthermore, a better understanding of matrix acidizing can lead to savings in time and resources during production operations.

1. INTRODUCTION
Production from unconventional oil and gas reservoirs especially shales has increased drastically in the past few years. Unconventional reservoirs are characterized by extremely low permeability (micro- to nanodarcy) which is why various stimulation treatments are being implemented to produce from such tight reservoirs such as multistage hydraulic fracturing. Substantial decrease in production rates (around 90%) of these reservoirs has been reported in the initial 3 years. The recovery factors were found to be 25% and 10% for gas and oil reservoirs, respectively, despite the implementation of hydraulic fracturing stimulation and horizontal drilling. Very high breakdown pressure in shale reservoirs is one of the major challenges at sites due to the extremely low permeability. Furthermore, the requirement of a huge amount of water for hydraulic fracturing stimulation is another challenge especially in the areas of water scarcity such as in the Middle Eastern countries.
Formation breakdown pressure of oil and gas reservoirs is usually reduced using acidizing treatment. Two types of acidizing treatment are employed to enhance the production rates and permeability of reservoir rocks: acid fracturing and matrix acidizing. In matrix acidizing, wellbore is stimulated by acid injection keeping the injection pressure lower than the fracturing pressure of the formation. Acid reacts with the carbonate minerals which in turn enhances the permeability (by enlarging the pore throats) of the rocks around the wellbore and removes the wellbore damage. An increase in production of 10–100 times can be made possible after the removal of near wellbore damage. Removal of damage considerably increases the production rate. On the other side, in acid fracturing acid is injected at a pressure higher than formation breakdown pressure for the creation of fractures in the undamaged formations.

Among all of the acid types used for acidizing treatment, the most commonly used acids are inorganic ones such as HF/HCl and HCl. In general, HCl is widely used to enhance the permeability of carbonate rich shale and carbonate formations. Eagle Ford shale and Marcellus shale are typical examples of carbonate rich shale. The rate of reaction of HCl is faster at a higher temperature and almost double in the case of limestone at 60 °C as compared to that at the room temperature (27 °C). In some cases, HF is used to stimulate the reservoir formation as well. Furthermore, weak organic acids are applied under certain conditions. Highly permeable conductive channels are formed in the formation as a result of matrix acidizing to enhance the flow of fluids toward the wellbore.

Several studies have been conducted to investigate the effect of matrix acidizing on shale formation. Significant increase in the permeability (from nanoDarcies to microDarcies) was observed as a result of matrix acidizing on Eagle Ford shale using 15% HCl. An experimental study was conducted by Morsey et al. to investigate the effect of HCl acid on pore volume, crack distribution, and imbibition in different shale formations including Marcellus shale, Mancos shale, Barnett shale, and Eagle Ford shale. Experiments were conducted using different concentrations of acid, that is, 4%, 15%, and 20%. Results demonstrated that performance of 4% HCl was optimum in terms of porosity enhancement and hydrocarbon recovery without destroying the pore structure of the rock formation. A reduction in the uniaxial strength by 27–70% and Young’s modulus by 25–58% was observed in these samples. An experimental study was conducted on matrix acidizing of Eagle Ford shale by Tripathi and Pournik, which resulted in a significant increase in the effective porosity as a result of 38% dissolution of the core samples after treatment with 15% HCl solution. Grieser et al. investigated and reported the alteration in mineralogy and microsurface structures of the shale rock after the treatment with low concentration HCl. Acidizing treatment causes the complexity to shale microstructures.

Various aspects of matrix acidizing on Eagle Ford shale were investigated by Khalil et al. using oil saturated core samples. The results revealed that 15% HCl is the optimum concentration for the acidizing treatment of shale. Acidizing treatment caused the width of fractures to increase in addition to the permeability enhancement. Wu and Sharma conducted an experimental program to evaluate the effects of matrix acidizing on Bakken shale. HCl (3 wt %) treatment caused the dissolution of Bakken shale by almost 35% by weight. Mechanical properties and pore structures were also altered as a result of acidizing treatment. Creation of macropores enhanced the fracture conductivity and pore volume. Fracture surface hardness was also reduced by 30–70%.

Effect of acidizing treatment with 1% and 3% HCl was studied on porosity and permeability of 48 shale samples, from three different shale formations. Significant increase in the porosity and permeability of shale cores was observed after treatment with 1 and 3% HCl for 4 days. A study was conducted on Longmaxi shale and Yanchang shale formations to investigate the effects of HCl acid treatment for 2 h using 15% HCl mixed with 3% KCl solution. Analysis revealed the increase in pore connectivity through creation of cracks. Singh et al. performed the stimulation treatment in the laboratory on the Eagle Ford shale with different concentrations of HCl (0.5–15 wt %). Experiments showed an increase in fracture conductivity by 4000% after the acid treatment.

Hardness of different shales including Utica, Haynesville, Eagle Ford, and Barnett shales were substantially reduced by 54.5% as a result of acid etching. Surfaces of shales with high carbonate contents were found to be more etched indicating that the surface etching corresponds to the carbonate dispersal pattern. A simulation was also performed to study the effect of carbonate contents on acid fracturing. Results exhibited that channels are formed due to the presence of thick fingering pattern of carbonate veins inside the shale rock samples. Marcellus shale contains high carbonate contents; acidizing treatment works well for this shale formation. Piane et al. and Gupta and Mishra reported 80–90% and 75%, respectively, of calcite mineral in form of calcite clasts and calcite veins in the Marcellus shale which makes it a suitable formation for matrix acidizing treatment. Matrix acidizing results obtained in the laboratory experiments might not represent the acidizing process at the reservoir scale. However, laboratory results could be used as a framework to guide field operations. An experimental study was conducted to investigate the various aspects of acid treatment and its impact on porosity, permeability, chemical reaction rate, acid penetration rate, and solubility at reservoir temperature of 66 °C and pressure of 10.35 MPa.

Extensive research on acidizing treatment on shales has been reported in literature outlining the changes in petrophysical and microstructural changes in various shale formations as a result of acidizing treatment. Furthermore, limited literature is also available on the impact of acidizing treatment on static Young’s modulus (YM) and breaking strength of shale. However, no literature is available on impact of acid concentrations and treatment time on various mechanical properties such as rock strength (continuous UCS profile), rock surface hardness, acoustic velocities, dynamic elastic parameters, YM, and Poisson’s ratio (PR), which is the primary focus of this research. Furthermore, microimaging, medical computed tomography (MCT) scanning, and mineralogical composition were analyzed to strengthen the results of acid impact on mechanical and physical properties.

In this study, a unique approach was adopted to investigate the impact of acid treatment on deterioration of mechanical integrity in terms of scratch strength (continuous profile of uniaxial compressive strength (UCS)), rock surface hardness (RSH), dynamic YM, PR, acoustic velocities (compressional and shear-waves), and brittleness index. Furthermore, changes in mineralogical composition, microscale surface features, porosity, and permeability were also studied. The study was conducted on Eagle Ford shale core plugs using different concentration of HCl acid: 0% (brine with 3% KCl solution),
Table 1. Initial Measurements of Rock Properties

| property | porosity (fraction) | permeability (nanodarcy) | UCS (MPa) | RSH (GPa) | YM (GPa) | PR | \( V_p \) (m/s) | \( V_s \) (m/s) |
|----------|---------------------|--------------------------|-----------|-----------|----------|----|----------------|----------------|
| minimum  | 0.034               | 0.10                     | 88.75     | 57.4      | 57.6     | 0.234 | 5372           | 3145           |
| maximum  | 0.069               | 1.08                     | 90.02     | 59.5      | 59.2     | 0.245 | 5398           | 3163           |

2%, 4%, 6%, 10%, and 15% HCl acid solution prepared in 3% KCl solution. Two important aspects were mainly covered in this study, that is, impact of different acid concentrations and treatment time on rock properties.

2. MATERIALS AND METHODS

2.1. Rock Samples. Eagle Ford shale was selected for this study. Core plugs of 2 in. in length and 2 in. in diameter were prepared after the cutting and grinding processes. Both endfaces of cores were ground to make them parallel and smooth for accurate determination of the rock properties. The mineralogical composition of carbonaceous-rich Eagle Ford shale was determined by X-ray diffraction (XRD). Basic measurements of core plugs (dimensions, weights, volumes, etc.) were determined before applying the acid treatment. Shale cores were subjected to the static acid dissolution treatment using different concentrations of HCl acid such as 0%, 2%, 4%, 6%, 10%, and 15% mixed with 3% KCl solution. For each acid concentration, core plugs were treated for three selected times, that is, 10, 20, and 30 min, to study the impact of treatment time on the mechanical properties. Mass loss for the core samples was computed from the difference in weights before and after the treatment.

Variation in the rock properties was monitored and investigated through various measurements and analyses such as porosity, permeability, scanning electron microscopy, high-resolution medical computed tomography (MCT) scanning, scratch strength (uniaxial compressive strength), rock surface hardness, acoustic velocities, dynamic elastic parameters, and brittleness index. All the mentioned measurements were conducted before and after the acidizing treatment of core plugs.

Uniaxial compressive strength (UCS) was determined using the scratch test system that provides a continuous profile of UCS for the whole core length from one end to the other. Rock surface hardness was measured on the surface of core faces using the Autoscan system. Compressional (P) and shear (S) wave velocities were measured using acoustic measurement system of the scratch test machine. Dynamic rock stiffness (YM) and PR were computed using the measured P- and S-wave velocities and density. Furthermore, brittleness index of shale was determined on the basis of elastic parameters for the untreated and treated cores proposed by Rickman.29 30 Before the acid treatment, initial UCS, average rock surface hardness (RSH), YM, PR, and P- and S-wave velocities (\( V_p \) and \( V_s \)) were measured on a set of three core plugs. The summary of initial results is shown in Table 1.

2.2. HCl Acid Solution. In this study, HCl acid solutions were prepared with varying concentrations such as 0%, 2%, 4%, 6%, 10%, and 15% for the treatment of Eagle Ford shale. Acid solution was mixed with 3% KCl in order to avoid swelling of clay minerals. Two aspects of acidizing treatment were investigated in this study: impact of acid concentrations and treatment time on rock mechanical properties. Acid treatment was performed at three selected periods of time: 10, 20, and 30 min for each concentration of HCl acid in order to study the impact of treatment time on rock properties. All acid treatments were done at ambient temperature and pressure conditions.

2.3. Measurements of Rock Physical and Mechanical Properties. This study investigates the variation in porosity, permeability, mineralogical composition, microstructures, uniaxial compressive strength, rock surface hardness, acoustic velocities, and dynamic elastic parameters (YM and PR) as a result of acidizing treatment on Eagle Ford shale samples. The mentioned properties were determined for untreated and HCl treated shale core samples.

Porosity measurements were made before and after the acid treatment of core plugs. Porosity was measured using a porosimeter (APP-608) instrument. Core holder along with sleeves was used for core placement. A confining pressure of 500 psi was applied and was kept constant throughout the experiment. Porosity was derived using Boyle’s law (eq 1)

\[
P V = k \text{ (constant)}
\]  

where P and V are pressure and volume, respectively.

The pore volume was measured by allowing helium gas to expand at known conditions of pressure and temperature. Bulk volume was calculated using core dimensions, and porosity was computed from the ratio between the pore volume and the bulk volume.

Permeability at nanoscale was measured using nanoperm equipment manufactured by Corelab. The apparatus uses the steady-state flow method for determining the permeability of the sample. The sample was placed in the core holder and a confining pressure of 500 psi was applied. Nitrogen gas with a pressure of about 25 psi was injected into the sample, and the flow was allowed to reach a steady-state over the period of time (2–3 days). After that, the relevant pressure-time data is used to calculate the most representative permeability of the sample.

Mineralogical composition was determined using X-ray diffraction to study the compositional changes that occurred due to acid treatment. MCT was conducted to investigate the small-scale changes in core features. Whole core was scanned using X-ray at a resolution of 1 mm and for a range of computed tomography (CT) numbers. The selected CT number was attributed to the color contrast to highlight different features. In addition, microscale analysis was done using SEM to study microstructural changes as a result of acid treatment.

Scratch test system was used to measure the scratch strength and the comressional- and shear-wave velocities of core plugs before and after the acid treatment. Uniaxial compressive strength is equivalent to the scratch strength.30 Measuring the scratch strength has several advantages over the conventional UCS measurements. It is nondestructive, repeatable, easier, and a faster way of measuring the UCS.31

While scratching the surface or specimen, the cutter experiences the normal and tangential forces, \( F_n \) and \( F_t \), acting along the direction of cutting surface and perpendicular to it, respectively. As a result of scratching process, intrinsic specific energy \( E \) is determined from the measured forces which is actually the amount of energy required to break a unit volume of rock. The relationship between \( E \) and \( F_t \) is shown in eq 2 where \( A \) is representing the cross-section area. The scratch strength profile is shown in Results and Discussion.
Cutting depth mainly controls the mechanisms of two typical failure modes ductile and brittle. Depth of cutting is set accordingly to avoid the brittle mode of failure for precise determination of UCS. The scratch test provides a continuous profile of UCS from one end to the other.

The P- and S-wave velocities are determined using the acoustic measurement system of scratch test system using transmitter and receiver probes. Acoustic velocity measurements reflect the bulk properties of the core plugs. Measurements were done for treated and untreated core plugs at zero confining pressure. Transmitter and receiver probes are landed at different locations of core plugs to acquire the acoustic data. Dynamic elastic parameters were computed using eqs 3, 4, and 5:

\[
E_{\text{dyn}} = \rho V_S^2 \left( \frac{V_P^2}{V_S^2} - 1 \right) - 4 \left( \frac{V_P^2}{V_S^2} \right)^2
\]

(3)

The equation can be reduced to the following expression.

\[
E_{\text{dyn}} = 2\rho V_S^2 (1 + \nu)
\]

(4)

Dynamic Poisson’s ratio \(\nu_{\text{dyn}}\) is:

\[
\nu_{\text{dyn}} = \frac{\rho V_P^2 - 2\rho V_S^2}{2(\rho V_P^2 - V_S^2)}
\]

(5)

where \(V_S\), \(V_P\), \(\rho\), \(E_{\text{dyn}}\), and \(\nu_{\text{dyn}}\) are the shear wave velocity, compressional wave velocity, bulk density, dynamic YM and PR, respectively.

Rock surface hardness is another vital parameter to assess the rock stiffness and soundness. It was measured on the core faces by impact hammer test before and after the acid treatment. The same core face was selected for each measurement in order to compare the hardness of untreated and treated core plugs. Impact hammer test was carried out using the AutoScan system which is developed by New England Research Inc. (NER). The system provides the rock surface hardness in terms of YM by the nondestructive impact hammer test. The AutoScan system generates the force versus time curve that could be utilized to obtain the dynamic elastic properties of core plug. It uses a probe which lands at various locations of the core face for acquiring the hardness data.

Brittleness index (BI) of Eagle Ford shale was computed before and after the acidizing treatment using elastic parameters as the approach proposed by Rickman et al.\textsuperscript{29} Figure 1 shows the flowchart of the experimental procedure adopted in this study.

### 3. RESULTS AND DISCUSSION

#### 3.1. Acid Impact on Rock Mass, Porosity, and Permeability

The mass of the core plugs was reduced after each treatment cycle with HCl. The progressive loss of mass (average of three core plugs at each concentration) after the treatment with different concentrations of acid is shown in Figure 2. Acid reacts with the shale minerals and causes the rock mass to decrease. The loss in rock mass after the acid treatment for 30 min was recorded. Dissolution effects were also observed in core plugs through visual examination as shown in Figure 3. A loss of 1.46% in rock mass was recorded after 30 min of treatment with 15% acid solution. The dissolution effects are more pronounced at higher concentrations of acid solution, that is, 10 and 15%.

Considerable improvement was observed in porosity and permeability of core plugs after the treatment at each concentration and the highest was recorded at 15% concentration. Dissolution of calcite minerals created empty pores causing the porosity to increase. Created pore spaces due to dissolution may be visualized in core images as shown Figure 3. Porosity was enhanced from 3.41% to 9.86% after the treatment.
with 15% acid for 30 min. Permeability of shale in the vertical direction (perpendicular to the bedding planes) was increased after each cycle of treatment as shown in Figure 4. Maximum enhancement (increased from 0.1 to 900 nanodarcy) was observed after 30 min of treatment with 15% acid concentration.

Impact on Mineralogical Composition.

Mineralogical composition obtained from XRD revealed that the major minerals in Eagle Ford shale were calcite, quartz, illite, kaolinite, pyrite, and plagioclase (Figure 5). Mineralogical composition is changed as a result of HCl treatment. HCl acid reacted and dissolved the carbonate minerals (calcite and dolomite) which caused a significant reduction in the amount of calcite mineral as shown in Figure 5. Relative abundance of quartz and calcite minerals has changed from 21.2 to 44.9% and 58.6 to 46.1%, respectively, as a result of acid treatment.

Figure 3. Selected core plug showing acid dissolution effects: (A) untreated, (B) after treatment for 10 min, (C) after treatment for 20 min, and (D) after treatment for 30 min.

Figure 4. Porosity and permeability after 30 min of treatment for different acid concentrations.

Figure 5. Mineralogical composition of Eagle Ford shale from XRD before and after the HCl treatment.
Figure 6. SEM images showing morphology of minerals especially calcite and quartz before the acid treatment. Image resolutions are 5 μm (left) and 3 μm (right). Magnifications are 25 000× (left) and 40 000× (right).

Figure 7. Morphology of minerals under SEM after the acid treatment dominated by the quartz minerals. Image resolutions are 10 μm (left) and 5 μm (right). Magnifications are 10 000× (left) and 20 000× (right).

Figure 8. Medical CT scanned images of core plugs (A) before treatment and (B) after treatment.
Scanning Electron Imaging. Scanning electron microscopy (SEM) was conducted to study microstructural features of the shale samples before and after the acid treatment. The samples were coated with platinum prior to the SEM analysis which was conducted at different resolutions (from 1 to 50 μm) and magnifications (from 1000 to 40,000). Surface morphology exhibited that calcite was the most abundant mineral in Eagle Ford shale while quartz was the second major mineral. Calcite and quartz contents were 58.6% and 21.2%, respectively. Microstructures of calcite and quartz minerals before the treatment are shown in Figure 6. Post-treatment SEM analyses illustrated that quartz had become the dominant mineral after the treatment along with a relatively lower content of calcite as shown in Figure 7. Acid treatment dissolved a good amount of calcite, dolomite, and other sediment particles making the shale rougher and more porous (Figure 7). This in turn led to the alteration in physical and mechanical properties as well.

Medical Computed Tomography. Medical computed tomography (MCT) was performed to visualize the small-scale changes that had occurred due to acid treatment. Core plugs were scanned at 1 mm resolution and the CT number was kept between 1800 and 2200 to gain an optimum contrast. Reduction in UCS was increased from 11.4 to 15.2% with an increase in acid concentration. Increase in acid concentration exhibited that calcite was the most abundant mineral in Eagle Ford shale while quartz was the second major mineral. Calcite and quartz contents were 58.6% and 21.2%, respectively. Experimental results demonstrated that the UCS decreases as the concentration of acid increases from 0 to 15% HCl. Rock mechanical properties Eagle Ford shale. The initial UCS was found to be 89.8 MPa before the acid treatment. Experimental results demonstrated that the UCS decreases as the concentration of acid increases from 0 to 15% HCl. Rock strength (UCS) was measured after treatment at different concentrations from 0 to 15% to analyze the changes occurred in strength characteristics.

The comparison of UCS profiles before and after the acid treatment resulted in a significant amount of reduction in UCS. UCS reduction is more profound at higher concentration. Effects of acid concentrations are demonstrated after 30 min of treatment with HCl. Average UCS of the core plugs was reduced from 89.8 to 46.7 MPa (48%) after treatment with 15% HCl acid. UCS was decreased by 11.4% as a result of treatment with 2% HCl acid and UCS was decreased from 89.8 to 79.8 MPa. Reduction in UCS was increased from 11.4 to 15.2% with an increase in acid concentration. Increase in acid concentration increases the acid dissolution effect in the core plugs which is one of the primary reasons of the weakening effect after treatment. Scratch strengths at different acid concentrations are demonstrated in Figure 9. The continuous UCS profiles, average UCS, and core images after the treatment with each concentration are also shown in Figures 10 and 11.

Acid treatment time was found to be an important aspect contributing to the strength reduction of the shale cores. For each acid concentration, treatment was performed for three different durations, that is, 10, 20, and 30 min. Two important scenarios were observed while studying the treatment time effect on strength deterioration. At higher acid concentrations, the deteriorating effect of acid was noticeably higher during the first 10 min of treatment as indicated by relatively steeper slope (Figure 9). The rate of UCS reduction for the next 20 min was...
found to be relatively slower. For instance, core plugs exhibited a UCS decrease of 37.6% after the acid treatment for 10 min that cause the major strength reduction and continue to further decrease (total reduced by 48%) with the treatment time. It means substantial reduction of 37.6% in UCS was caused during the first 10 min of acid treatment and further 10.5% reduction took place in next 20 min of acid treatment. Therefore, rate of UCS reduction was higher at the start of treatment which decreased with the passage of time. Hence, acid dissolution rate is also faster for the first 10 min and relatively slow with later times. Likewise, for the 10% concentration case the UCS was deteriorated by 27.2% for first 10 min as the strength decreased from 89.8 to 65.4 MPa and further decreased by 12.6% in next 20 min, reducing from 65.4 to 31.8 MPa.

On the contrary, a quite different scenario was observed for treatment time at low acid concentrations. During the first 10 min of acid treatment at lower concentration, strength deteriorating effects are not very significant, causing the decrease in UCS at a slower rate, followed by a significant reduction at a faster rate for the next 20 min. For the case of 2% concentration, UCS was reduced from 89.8 to 86.7 MPa (3.5%) after 10 min of treatment, followed by a decrease from 86.7 to 79.8 MPa (~8%) for the next 20 min (Figure 9). At low concentrations, initially acid dissolution was relatively efficient and slower as substantial UCS reduction was observed to have taken place after the treatment for 30 min.

The results provide very useful information for fracturing treatment of tight shale formations. The reduction in compressive strength leads to a reduction in the breakdown pressure. A better understanding of acid treatment will be helpful in designing better ways to improve productivity in shale reservoirs.

3.3. Impact on Rock Surface Hardness (Impulse Hammer). Rock surface hardness (RSH) was determined on the flat face of the core plugs before and after acid treatment. Considerable decrease in the rock surface hardness was observed after each cycle of treatment. The average rock hardness in terms of YM was reduced by 14.8, 24.1, 36.9, 51.7, and 64.6% after the treatment with acid concentrations of 2, 4, 6, 10, and 15%, respectively (Figures 12 and 13). Rock hardness exhibited a sharp decrease at high acid concentration and gentle decrease at lower concentration of acid similar to the trends observed in the case of rock strength. A sharp decrease indicated higher rate of dissolution and vice versa.

The post-treatment results revealed that acid concentration has a pronounced impact on the RSH causing a considerable
reduction. Decrease in RSH was observed to be nonlinear with increase in acid concentration. As the concentration increases, dissolution effects become more pronounced causing the reduction of RSH at a higher rate. A relative decrease in RSH reduction was increased by 9.2% and 12.7% when acid concentration was increased from 2 to 4% and 4 to 6%, respectively. Treatment with 15% acid resulted a decrease of 64.6% (reducing from 58.4 to 20.7 GPa). The concentration and time impact on RSH decrease is shown in Figures 12 and 13.

The RSH was decreased by 3.0% after the treatment with 2% concentration for 10 min following the increases of 14.8% in next 20 min. With the increase in acid concentration, RSH reduction rate was observed to be increased for the first 10 min of acid treatment. After the treatment with 4% concentration for 10 min, 10% reduction in RSH was noticed whereas total RSH reduction was 24.1% reduction after 30 min. However, the effect of even low concentration (2% and 4%) was quite significant which caused the RSH to reduce by 14.8% and 24.1%, respectively Figure 12 exhibited the decrease in RSH for different concentrations and treatment time. Decreasing the trend is slightly changed when concentration increases from 4 to 6%. For the first 10 min, 24.3% reduction happened followed by the 12.4% further reduction in next 20 min of treatment. An increase in concentration caused the faster deterioration of RSH due to higher dissolution rate.

In comparison, deterioration of RSH was relatively faster in the case of 10 and 15% HCl treatment which led to speedy reduction of RSH. After the 10 min, 39.6 and 48.1% reduction was observed in RSH indicating very high dissolution rate due to high concentrations (10% and 15%) as shown in Figure 13. Next 20 min of treatments caused the RSH reduction of 12.2% and 16.4% at 10% and 15% concentrations, respectively. One of the possible reasons for the high rate of acid reaction is the high contents of calcite minerals in Eagle Ford shale which are susceptible to react with HCl acid. Hence, a substantial change happened in shale core plugs in terms of RSH.

3.4. Acid Impact on Acoustic Properties. Acoustic velocities were also measured for all the core plugs after the acid treatment at the concentrations of 0%, 2%, 4%, 6%, 10%, and 15%, respectively. Acoustic measurements revealed a remarkable alteration in bulk properties of Eagle Ford shale. Compressional (P) and shear (S) wave velocities were measured without applying confining pressures. P- and S-wave velocities were measured as 5383 and 3155 m/s, respectively, before the acid treatment. Acid treatment caused a substantial decrease in P- and S-wave velocities as exhibited by the post-treatment
results. Acid dissolution enhances pore spaces which is one of the major reasons for decrease in P- and S-wave velocities. Acid dissolution slowed down the P- and S-wave velocities which in turn reduced dynamic elastic parameters (YM and PR).

Results demonstrated a decrease of 5.46% and 7.1% in P- and S-wave velocities, respectively, after 2% acid treatment. P- and S-wave velocities were reduced in a similar manner, however, reduction rate of S-wave velocity was more profound because of acid dissolution. Increase in concentration led to the increase in velocity reduction rate because dissolution impact is more significant at higher concentrations, although the relationship is nonlinear. The P- and S-wave velocities reduction with acid concentrations and treatment time are demonstrated in Figures 14 and 15.

A study of velocity reductions revealed that the reduction factor is different at different times of treatment. Acoustic velocities exhibited major deterioration in both velocities during the first 10 min of treatment. However, acid impact on S-wave velocity reduction was slightly more prominent which might be caused by the increase in pore spaces. A slight change in pore
spaces considerably affects the travel times of acoustic waves. P- and S-wave velocities were decreased by 3.8% and 4.3%, respectively, after treatment with 2% acid solution for 10 min followed by the further decrease of 1.6% and 3.8%, respectively, in the next 20 min. This peculiar behavior is slightly different from the reduction behavior of YM and RSH described in previous sections.

Similar reduction behavior in P- and S-wave velocities was observed at higher concentrations. For instance, at 10% and 15%, P- and S-wave velocities were reduced to 4330 and 2256 m/s after 10 min which demonstrated 85 and 84% reduction of total reduction happened. The remaining 15% and 14% reduction in velocities took place in the following 20 min of treatment. The figures clearly show that the first 10 min plays a crucial role in altering the properties for higher acid concentrations.

3.5. Impact on Dynamic Elastic Parameters. Dynamic elastic parameters, that is, YM and PR, were computed using acoustic velocities and density measured on the core plugs. Quantification of dynamic rock stiffness and deformation/failure behavior helps in understanding the rock mechanical behavior. YM and PR reflected a substantial change after acid

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**Figure 14.** Reduction in P-wave velocity after acid treatment.

**Figure 15.** Reduction in S-wave velocity after acid treatment.
treatment at different concentrations. Dynamic rock stiffness exhibited a decreasing trend with the increase in acid concentration from 0% to 15% as shown in Figure 16.

Rock stiffness was measured as 58.3 GPa before the acid treatment. Major reductions were observed at higher concentrations, that is, at 10% and 15% which were 38.5% and 50%, respectively. Results revealed that higher acid concentrations (10% and 15%) contribute more effectively to deteriorating the resistance of the rock to the applied stress. The stiffness was decreased with an increase in acid concentration in a nonlinear manner. Results revealed that acid dissolution rate was different at each concentration. Impact of acid concentration and treatment time on the YM reduction is shown in Figure 16.

On the contrary, PR demonstrated an increasing trend with the increase of acid concentration. Before the acid treatment, PR was observed to be 0.238 which increased to 0.252 after treatment with 2% acid. PR continued to increase with acid concentrations nonlinearly. PR was highly influenced by the high concentrations. At low concentrations (2%), initial 10 min caused an increase of just 1.7% which continued to increase with treatment time and exhibited a total increase of 5.6% after 30 min. It means that 30% reduction happened during the first 10 min and 70% in the following 20 min as demonstrated in Figure 17. On the other hand, PR was increased by 24.8% after 10 min of treatment at 15% acid concentration. In this and most of the cases discussed above, it shows that the first 10 min plays a
crucial role in altering the properties. The higher the concentration is, the faster the reaction and the associated changes in properties are. Most of the acid concentration is consumed within the first 10 min and after that the reaction rate will diminish. The rate of change in properties after the first 10 min is similar to that for lower concentrations. The movement of H+ ions from the acid to rock surface may also be inhibited by the products of the reaction that takes place within the first 10 min.

Deformation under axial stress/load is highly affected by the acid dissolution at high concentrations (10% and 15%) which might impact the rock fracturing treatment in Eagle Ford shale. Increase in PR reflects the transition of mechanical behavior of the shale with more tendency to deform laterally under axial stress. It also implies that the rock is becoming more incompressible with the exposure to acid with respect to the role of Poisson’s ratio. However, overall compressibility is a function of the decrease in stiffness too. The response of shale to the applied stress is changed significantly after the treatment as a result of decrease in stiffness. Hence, deformation pattern and resistance to failure is also different after the acid treatment. Table 2 shows the summary of changes in rock mechanical properties after acid treatment.

### 3.6. Acid Impact on Brittleness Index

A significant decrease in BI was noticed for the acid treated samples. BI was observed to be reduced after each run of treatment. After the treatment with 2% acid, BI was reduced by 15.4%. Treatment with 4% and 6% acid caused a reduction of 21.5% and 40.9%, respectively. Reduction in BI was more evident for a change of concentration from 4 to 10% indicating by steep slope in Figure 18.

| acid concentration (%) | avg. UCS (MPa) | relative UCS reduction (%) | avg. hardness (GPa) | relative hardness reduction (%) | avg. YM (GPa) | relative YM reduction (%) | avg. PR | relative PR reduction (%) |
|------------------------|----------------|---------------------------|--------------------|-----------------|----------------|-------------------------|--------|--------------------------|
| 0                      | 89.8           | 58.4                      | 58.4               | 21.5            | 58.3           | 64.6                    | 0.238  | 55.5                     |
| 2                      | 79.8           | 15.2                      | 49.8               | 12.7            | 50.9           | 35.8                    | 0.252  | 47.2                     |
| 4                      | 76.2           | 26.1                      | 36.9               | 13.9            | 47.7           | 23.7                    | 0.258  | 8.3                      |
| 6                      | 66.4           | 25.4                      | 28.2               | 11.4            | 40.4           | 18.7                    | 0.275  | 15.4                     |
| 10                     | 54.1           | 39.8                      | 36.9               | 12.7            | 35.8           | 38.5                    | 0.292  | 22.7                     |
| 15                     | 46.7           | 48.0                      | 28.2               | 12.7            | 29.2           | 49.9                    | 0.314  | 31.6                     |

“avg. stands for average values.

When concentration was increased from 4% to 6% and 6% to 10%, the reduction in BI was increased by 19.4% and 22.1%, respectively. Maximum reduction was observed in BI after the treatment with 15% acid. Similar to previous trends observed, BI also exhibited a sharp decrease at higher acid concentration and vice versa. Impact of acid concentration and treatment time is shown in Figure 18.

### 4. CONCLUSIONS

A detailed experimental study was conducted to investigate the impact of acidizing treatment on physical, compositional, and mechanical properties of Eagle Ford shale. Additional focus was given to two important aspects of acid treatment, viz., acid concentration and treatment time. The outcomes of the study are summarized below:

1. Porosity and permeability of the shale exhibited a noticeable enhancement. Porosity increased from 3.4% to 9.86% (almost three-fold) and permeability increased from 0.1 to 9.86 nanodarcy. HCl caused the dissolution of rock minerals and sediments which in turn enhanced pore spaces as well as pore throats. The study of mineral composition before and after the treatment confirmed the dissolution of major mineral, calcite, and other minor minerals. SEM analysis has also confirmed the porosity change due to mineral dissolution and compositional changes.

2. High-resolution MCT images confirmed that the laminae in which dissolution took place were mainly composed of calcite with small fractions of dolomite. The laminae composed of clay minerals were not very affected by the acid treatment.

3. Treatment time enhanced the dissolution of carbonaceous minerals. The rate of dissolution is mainly controlled by the acid concentration. Reaction rate was higher in the first 10 min for higher acid concentrations and therefore significant changes in properties were noticed for such cases.

4. Results revealed that the impact of higher acid concentrations was more pronounced on strength reduction compared to that for lower concentrations. The UCS of the shale was reduced by 48.0% after the treatment with 15% acid concentration.

5. The rock surface hardness (RSH) also exhibited a negative nonlinear relationship with increasing acid concentration. Higher acid concentrations resulted in a sharp decrease in rock hardness. A maximum reduction of 64.6% was observed after 15% acid treatment for 30 min.
6. Considerable changes in acoustic velocities were observed even at low acid concentration indicating that pore spaces have significant impact on the acoustic velocities.

7. Rock stiffness and brittleness index revealed a negative nonlinear relationship with acid concentration. Poisson’s ratio exhibited a positive nonlinear relationship indicating that the rock is becoming more incompressible with respect to the role of Poisson’s ratio when exposed to higher acid concentrations. However, overall compressibility is controlled by the decrease in stiffness, too.

The study outcomes will be helpful in deciding optimum acid concentrations and time for acidizing treatment in the Eagle Ford shale and other similar formations.

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**Notes**

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