Chapter

Swelling Behavior of Elastomers under Water, Oil, and Acid

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There are three principal means of acquiring knowledge: observation of nature, reflection, and experimentation. Observation collects facts; reflection combines them; experimentation verifies the result of that combination.

Denis Diderot

Abstract

It is very important to determine the behavior of elastomer materials under realistic well conditions in order to select appropriate swelling elastomers for a particular set of field conditions, for successful modeling and simulation of various downhole processes, and for design improvement of swell packers and other sealing applications. In collaboration with national and regional petroleum development and rubber engineering companies, a series of experimental studies were therefore conducted at Sultan Qaboos University for characterization of swelling related material behavior of different elastomers. Results from some of these investigations (studies A, B, and C) are reported and discussed in this chapter.

Keywords: swelling behavior, water-swelling, oil-swelling, acid induction

1. Introduction

It is very important to determine the behavior of elastomer materials under realistic well conditions in order to select appropriate swelling elastomers for a particular set of field conditions, for successful modeling and simulation of various downhole processes, and for design improvement of swell packers and other sealing applications [1]. In collaboration with national and regional petroleum development and rubber engineering companies, a series of experimental studies were therefore conducted at Sultan Qaboos University for characterization of swelling related material behavior of different elastomers. Results from some of these investigations (studies A, B, and C) are reported and discussed in this chapter.

2. Experimental setup

There are standard procedures for conducting most of the tests on rubber materials. It is important to follow these procedures carefully in conducting the tests in order to obtain consistent results. Methodology of the swelling test was developed in consultation with petroleum engineers and rubber manufacturers. Other

experiments were designed and performed in line with standard ASTM test methods. Apart from regularly available testing equipment, some simple test rigs and fixtures were designed and fabricated. The tests include swelling behavior (volume, thickness, and hardness change), compression set, tensile set, and tensile properties. Values of test temperature, water salinity, oil viscosity, and acid concentration were selected to emulate actual well conditions in different local oilfields.

2.1 Sample types

Plate samples are used to mimic the actual response of a swell packer (rubber element vulcanized onto a petroleum casing). These generally consist of 6 mm thick elastomer mounted on approximately 50 x 50 x 2.5 mm steel plates. As a basis for comparison, disc samples (28 mm diameter, 12 mm thickness) are used to assess the behavior if the elastomer is allowed to swell freely in all directions. It is very difficult to prepare standard dumbbell shape tensile specimens from elastomer sheet material, as the material is really flexible and not firm. It is far easier to perform tension test using ring samples, in accordance with ASTM standards. All sample elastomer materials are provided by different regional oilfield operators and rubber companies.

The three sample geometries are shown in **Figure 1**. Disc samples represent free swelling, and are used to measure compression set, swelling volume and thickness, hardness, and compression and bulk properties. Plate samples characterize restricted swelling (to replicate actual seal behavior; elastomer mounted on pipe); and are used to measure swelling volume, thickness, and hardness. Ring samples are used to measure tensile set, and tensile properties.

2.2 Sample preparation

Elastomer samples (in finished form) are sometimes supplied directly by rubber manufacturers, but are mostly prepared in-house. If swell packers (elastomer mounted on a base pipe) are provided, pipe is cut into sections on a lathe machine, and pipe sections are cut into desired plate samples using milling or saw cutting machine. To get disc and ring samples, elastomer is removed from the packer, and surface grinding is done on these sheets to smooth out the roughness, and to get the required thickness. If the elastomer is supplied as sheets, square or rectangular pieces of requisite size are cut, and then mounting/vulcanizing on pre-cut steel plates is done using specific glues. Disc and ring samples are cut directly from the sheet. **Figure 2** shows the various steps involved in sample preparation.

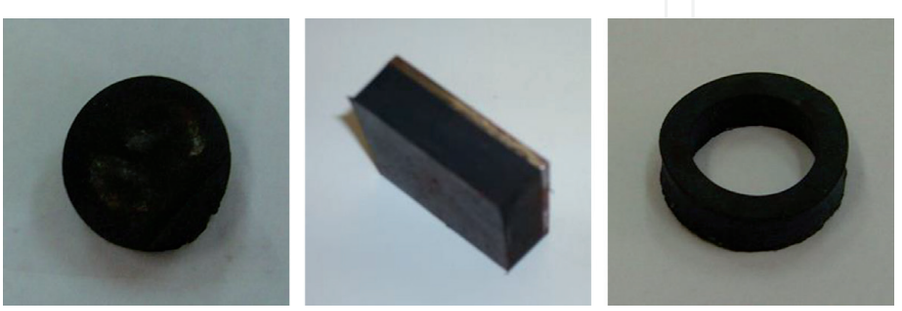

Figure 1.
The three sample geometries used for elastomer testing: Disc, plate, and ring.

Figure 2.
Different stages in sample preparation: Cutting sections from packer, and plate samples from sections; removing elastomer from pipe; surface grinding; cutting discs and rings using die-and-punch set.

2.3 Swelling medium

For water-swelling elastomers, salt-water solutions of different concentrations are prepared inhouse. For oil-swelling elastomers, actual crude oil from regional oilfields is procured from petroleum companies. For acid testing, HCl solutions of requisite concentration are prepared inhouse. Total testing time varies from one to three months. Swelling measurements are taken at different intervals, such as on day-zero (before swelling), and after 1, 3, 4, 7, 15, and 31 days of swelling.

2.4 Hardness test

An instrument called a durometer is used to determined hardness of rubbers and elastomers; **Figure 3**. A blunt indenter point is pressed into the sample surface (without causing any puncturing), and the instrument measures the resistance to penetration through the action of a spring. In analog models, movement of a pointer across a scale to indicates the resistance to penetration. The Shore Durometer is scaled from 0 to 100, higher numbers representing higher hardness. The two commonly used scales are "A" for soft rubbers and "D" for harder materials. Applicable test standard is *ASTM D2240* [2]. Room temperature hardness values reported here are average of five readings taken at different locations on the same each sample.

Figure 3.
Durometer for hardness testing.

2.5 Compression set test

Compression set is a measure of the ability of a rubber or elastomer to retain elastic properties after prolonged action of compressive stress. The test is run for either 22 hours or 70 hours. The height that is not recovered represents the compression set, reported as a fraction (percentage) of the amount by which a standard test sample fails to return to its original thickness when acted upon by a standard compressive force/deflection for a predetermined time period at a specific temperature. Following ASTM guidelines (*ASTM D395, method B*) [3], a dedicated fixture was designed and fabricated in-house for the compression set test of disc-type elastomer specimens (13 mm diameter, 6 mm thickness); **Figure 4**. Each test is carried

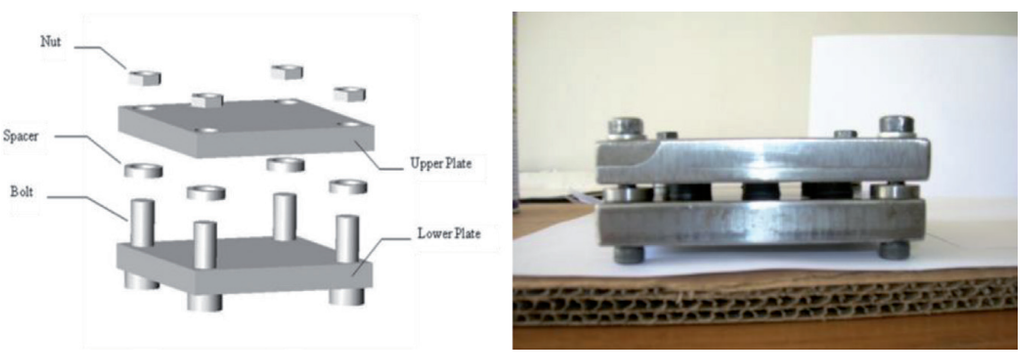

Figure 4.
Test fixture for compression-set test, fabricated in-house.

out at a specified temperature. Samples are then removed to room temperature and allowed to cool for 30 minutes before thickness measurements. Rubbers having god resistance to compression set recover significantly upon releasing the load. 100% recovery is not necessary for an elastomer to work as an effective and repeatable seal. Moreover, if there is a constant compression on the seal, material recovery is not very important.

2.6 Tensile set test

When a specimen is stretched to twice its original size (100% stretch) for a stipulated time, then allowed to recover for the same time at room temperature, the remaining amount of extension determines the tensile set value. A special tensile fixture was designed and fabricated (in line with ASTM guidelines) for this test; **Figure 5**. Applicable standard is *ASTM D412* [4].

2.7 Tensile properties test

This test is used to quantify elastomer behavior under axial tensile loading at room temperature. After the resulting data is plotted as a stress–strain graph, tensile properties can be evaluated; such as modulus of elasticity, tensile strength, and % elongation (or % area reduction). Apparatus used is a universal testing machine fitted with a small load cell for rubbers and elastomeric materials, specially designed and fabricated hook-type grips to hold ring samples (in line with ASTM guidelines), data acquisition and recording system, and ring-type elastomer specimens (16 mm inside diameter and 3 mm thickness); **Figure 6**.

The following test procedure is carried out. Universal testing machine is carefully calibrated. Elastomer ring is mounted into the universal testing machine, using hook-type fixture. As specified in ASTM D412 [4] test standard, machine is set for a speed of 500 ± 50 mm /min. Values of the applied force and consequent elongation are recorded. Average readings from three samples are tabulated, and converted to stress–strain plots. From the data and graphs, tensile properties are calculated.

2.8 Swelling test

The objective of the test is to find the amount of progressive swelling (volume and thickness) and density change in an elastomer for a specified test period, and at different temperatures. Water-swelling elastomers are exposed to salt solutions

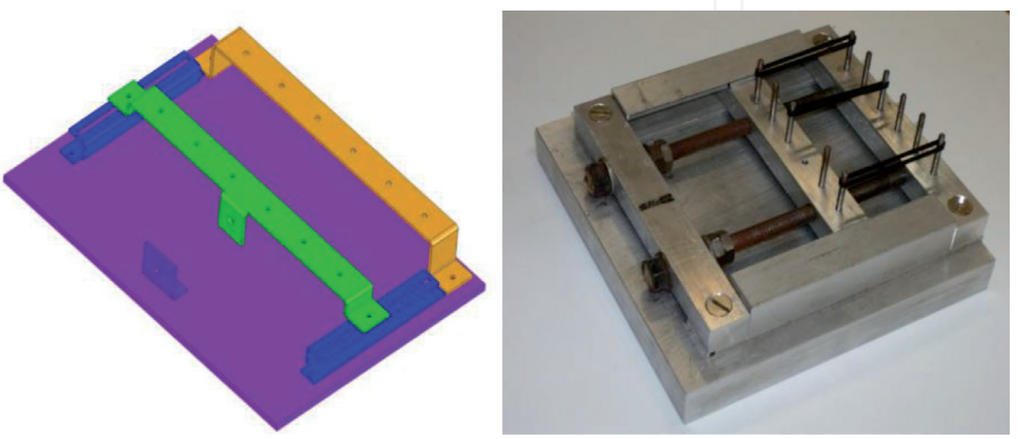

Figure 5.
Test fixture for tensile-set test, fabricated in-house.

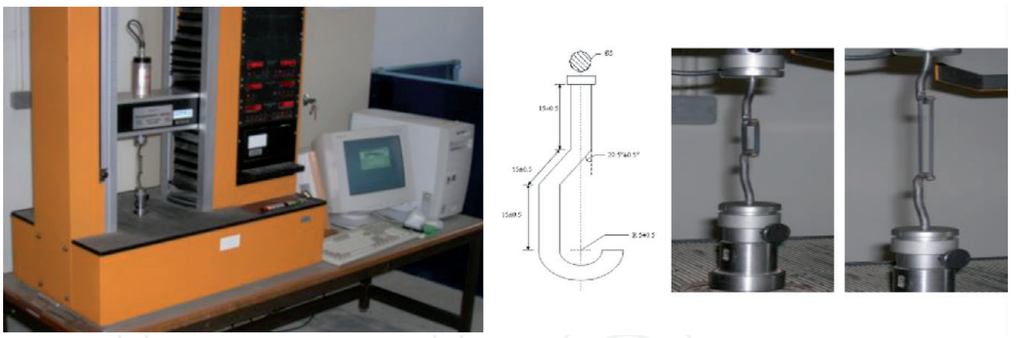

Figure 6.
Apparatus for tensile testing: Universal testing machine with data acquisition system, and hook type fixture for ring samples.

of different concentrations (ranging from 6,000 ppm or 0.6%, to 200,000 ppm or 20%), while oil-swelling elastomers are immersed in crude oils of different viscosities. Disc samples are used to study the swelling response of free (unconfined) elastomer, while plate samples (elastomer vulcanized onto steel plate) are used to replicate the sealing behavior of elastomer mounted on a pipe. Samples are placed in temperature-resistant sealable glass jars containing proper swelling medium (brine, oil, acid), utilized to maintain constant concentration even at higher temperatures. Each jar is identified by mnemonic code name. Jars are placed inside servo-controlled ovens maintained at prescribed temperatures throughout the test period. Thickness, volume, and mass (density = mass / volume) of each specimen are measured before swelling, and periodically after swelling under different conditions. Based on the displacement method, a special apparatus was designed and fabricated (consisting of glass beakers and graduated cylinders) for accurate volume measurements. Digital Vernier calipers are used for thickness measurements, while mass is recorded using a digital balance. Due to the toxic nature of crude oil, special care has to be taken in handling and ventilating the test area in the case of oil based elastomers. Various components of the swelling test setup are shown in **Figure 7**.

3. Study-A: Inert vs. swelling elastomer

This study is based on experiments conducted on mechanical testing and characterization of an inert (non-swelling) and a water-swelling elastomer (both belonging to the EPDM family) used for sealing purposes by a local petroleum development firm. The experiments are designed to study the effect of brine concentration, operating temperature, and sheet thickness on swelling and other properties of the elastomer. Tests were conducted to evaluate hardness, compression set (different temperatures and time periods), tensile set (different time periods), tensile properties (strength at fracture, % elongation), and swelling behavior. Swelling tests were conducted on different sample geometries, for both free and plate-mounted samples, in brine solutions of varying concentrations and at different temperatures. Total test duration was 1000 hours (about 45 days).

3.1 Experimental work

Both EPDM-type elastomers (water-swelling EPDM1, and inert EPDM2) were provided by a local petroleum development firm in the form swell packers: specified lengths of 5½ mm thickness mounted on steel pipe. Some of the elastomer sheets

Figure 7.
Different components of the swelling test apparatus.

were cautiously peeled off from the pipes. Thickness reduction for the elastomer sheets and the mounted elastomer was carried out on lathe machine and surface grinder, to match the required sample thickness. Saw-cutting and milling machines were then used to cut the mounted and free samples to requisite dimensions. Though ASTM standard sets forth a sample thickness of 6 mm, a thickness of 5 mm had to be used as the sheets had a pre-grinding thickness of 5½ mm. A dedicated die-and-punch set was used to cut the disc and ring samples. ASTM suggests rings of 18 mm OD and 1½ mm thickness; however, rings of 13 mm ID and 19 mm OD were used owing to the available punch sizes.

As discussed in published literature [5, 6] about the use of standard test methods, standards are set forth to ensure uniformity of test conditions in different locations. However, sample geometries are not always 100% binding, and a little leeway in dimensions is allowed if repeated results are consistent. Especially in the case of tensile/compressive testing, minor variations in sample dimensions do not cause any significant problems as stress is calculated per unit cross-sectional area. Forces causing the same amount of deformations are somewhat different due to the slightly different dimensions, but so is the area; net result of force per unit area (stress) remains the same. Moreover, at least three tests in each case also take care of the repeatability issue.

Reported hardness value in this work is the average of readings taken at five different locations on each sample. For the compression set test, test temperatures were room temperature (~25°C), 50°C and 80°C. For the tensile set test, ASTM standard test time is 10 min, but 10 hours and 20 hours were included to study variation of behavior more thoroughly. For tensile set and tensile properties test, ring samples were used (3 mm thickness, 3 mm width, and inside diameter of 13 mm). Disc samples (5 mm thickness, 13 mm diameter) were used for the compression set test. Hardness tests were done on 25 mm × 25 mm square samples of 5 mm thickness. Testing times were 1,000 hours (roughly 45 days) for swelling test; 10 min, 10 hours, and 20 hours for tensile set test; and 22 hours and 70 hours for compression set test.

For the swelling test, the objective was to find the volume or thickness change in salt solutions of two different concentrations (0.6%, and 20%), samples kept as three temperatures (room temperature, 50°C, and 80°C). Two types of test specimens were used. As unconfined samples (25 x 25 mm, 5 mm thickness; labeled 5 U) are not attached to any plate, and are free to swell on all sides, they give the swelling performance of free elastomer. On the other hand, samples mounted on steel plate (25 x 25 mm, 4 mm and 5 mm thickness, labeled 4 M and 5 M) are used to imitate sealing behavior of elastomer mounted on a pipe.

3.2 Results and discussion

3.2.1 Hardness

Measured hardness values (durometer Shore-A scale) ranged from 50 to 52 for the swelling elastomer EPDM1 (average 51.3) and from 59 to 62 for the inert elastomer EPDM2 (average 60.3). One reason for the slight variations in hardness values could be the peeling-off of elastomer sheets and subsequent grinding operations, giving rise to some non-uniformities. A swelling elastomer must be softer than a non-swelling elastomer (to allow water to seep in and make it swell), as confirmed by the measured hardness values.

3.2.2 Compression set

Figure 8 shows an increase in compression set CS (%) values with testing time and temperature. CS for EPDM1 (swelling type) is notably higher than that for the inert EPDM2, difference being more pronounced for longer test period and higher temperature. For the same elastomer material, 70-hour test values are higher than the 22-hour test. For EPDM1, CS values are not very different for room temperature and 50°C, but significantly higher for 80°C. We can infer from these values that permanent set would be large when the elastomer is compressed for a longer time at a higher temperature.

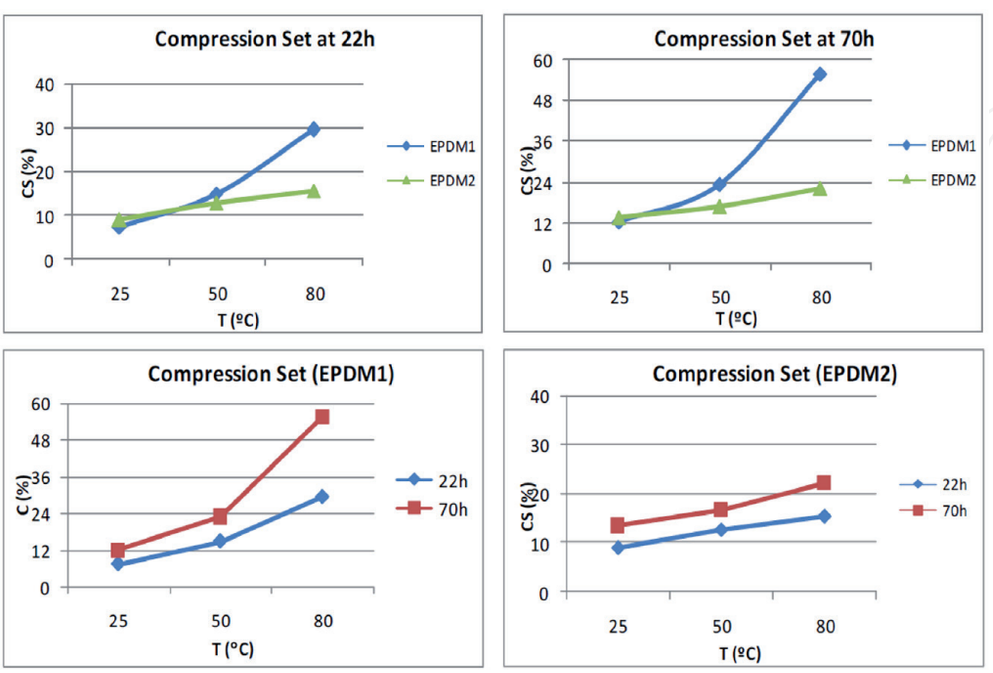

Figure 8.
Variation of compression set with testing time and temperature.

3.2.3 Tensile set

Figure 9 shows summarized values for the tensile set TS (%). As anticipated, TS values increase for longer testing time. This increase is more acute for the swelling elastomer EPDM1 than for the inert rubber EPDM2, as expected. ASTM test standard recommends a 10-min period for the tensile set test of rubbers. This appears to be too short for these much softer elastomers. Websites of many rubber vendors and manufacturers report the same testing time for both compression set and tensile set tests (22 hrs). Our in-house experiments were therefore conducted for test durations 10 min, 10 hour, and 20 hour, to have a better idea of how the behavior changes with time.

3.2.4 Tensile properties

Data from room-temperature tensile tests for both elastomer materials were converted into stress–strain diagrams; **Figure 10**. It is interesting to note that graphs for all three samples of EPDM1 nearly identical, and all curves are almost linear. This linearity makes the calculation of the slope much easier. We know that normal rubbers (like EPDM2) usually exhibit a nonlinear-elastic tensile behavior. The reason for the almost linear graphs for EPDM1 may be that swelling elastomers do not behave like normal rubbers due to their atypical cross-linking and special filler materials. For EPDM1 and EPDM2, average values of fracture stress (σ_f) were 36 MPa and 171 MPa, and of percent elongation (ε_f) were 265% and 371% respectively. Elastic modulus (E) for EPDM1 was 14.4 MPa, while it was not measured for the inert EPDM2 as the curve was nonlinear. Variation in readings for the three samples was 7%, 5% and 5% for σ_f, ε_f, and E respectively. Naturally, fracture stress and % elongation values for the far softer swelling elastomer EPDM1 are significantly lower than the inert elastomer EPDM2.

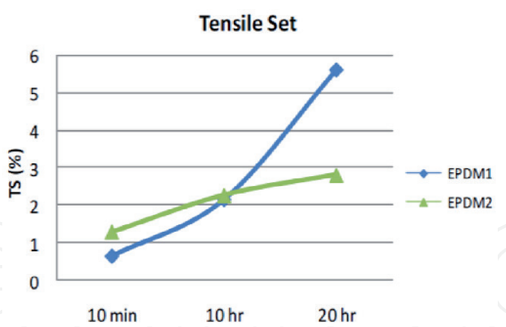

Figure 9.
Variation of room-temperature tensile set with testing time.

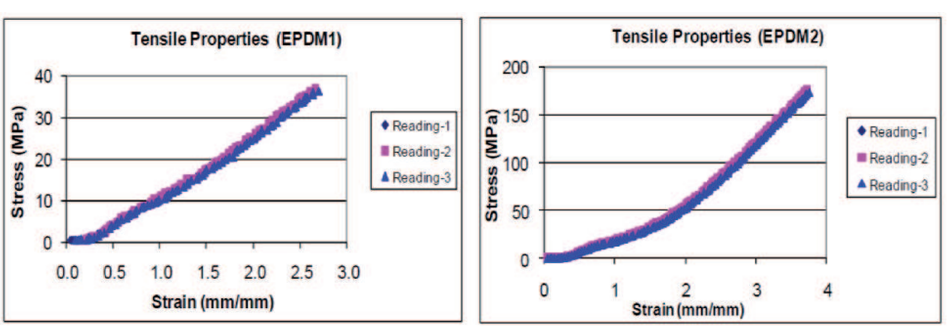

Figure 10.
Stress–strain plot from tensile test of three samples; both elastomers.

3.2.5 Swelling behavior

The most important test was of course about the swelling behavior of the elastomers. The inert elastomer (EPDM2) was of course a non-swelling type, and did not exhibit any notable changes in volume or thickness with time, as it was exposed to different saline solutions and temperatures. Graphs discussed here are therefore only for EPDM1, showing plots of swelling magnitude against time, expressed as volume change ($\Delta V\%$) and thickness change ($\Delta t\%$). Other parameters of interest are sample type and dimensions, salt concentration, and testing temperature. A systematic scheme is followed for the taxonomy (naming scheme). For example, (0.6%-80C) denotes solution of 0.6% salt concentration kept at 80°C temperature, while (4 M-50C) stands for a 4 mm-thick mounted sample tested at 50°C.

3.2.5.1 Volume change

All of the tests show that amount of swelling (in terms of % volume change) increases with increasing time. This is as expected; however, this increase is not continuous but behaves more like a step-curve: volume increases then remains constant for some time, then increases again; and so on. It is known that salt is one of the constituent materials for the swelling elastomer. As the elastomer samples are immersed in brine solutions, some salt enters into the elastomer body as water is absorbed. At the same time, small amounts of salt may also break away from the elastomer material and go into the salt solution. This two-way transport of salt means that swelling does not happen in a consistently increasing manner, but stops or even goes down for short periods of time before increasing again. Apart from the constituent materials (such as salt and other additives), one more very relevant factor in swelling elastomers is the cross-link chain density. With the breaking away of salt, some of the cross-links may be disturbed. This breaking and subsequent re-forming of cross-link chains in the elastomer may be another reason for the fluctuations in the amount of swelling [7].

If salinity value and temperature are the same, for instance 0.6% concentration and 80°C temperature (**Figure 11**), unconfined samples (5 U) exhibit higher swelling than plate-mounted samples (4 M and 5 M). It is clear that unconfined/unmounted samples are free to swell on all sides, while mounted pieces cannot swell on the surface that is restricted by the metal. If sample thickness is higher, it will obviously swell more. This is confirmed experimentally; 5 M samples show slightly more swelling than 4 M samples.

For same temperature and same sample type (eg. 4 M samples at 50°C; **Figure 11**), exposure to lower salt concentration (0.6%) generally yields higher swelling amount (volume increase). The is again an expected trend, since more concentrated and thicker solutions will not seep as much into the elastomer compare to the more dilute solutions. This will be true whether the swelling mechanism is diffusion or osmosis.

If salt concentration and sample configuration are the same (eg. 5 U samples in 20% solution; **Figure 11**), more swelling is observed at higher temperatures. This is also a natural behavior; more material expansion (swelling) and higher diffusion rates at higher temperatures.

3.2.5.2 Thickness change

Consistent with volume change behavior, it can be seen in all the graphs that sample thickness increases with swelling time. Once again, this increase is step-wise, though the fluctuation is smaller than for volume change. If salt concentration and temperature are kept constant (eg. 0.6% concentration and 50°C temperature; **Figure 11**), 5 M curve is higher than the 4 M curve, and the 5 U curve is noticeably higher than both

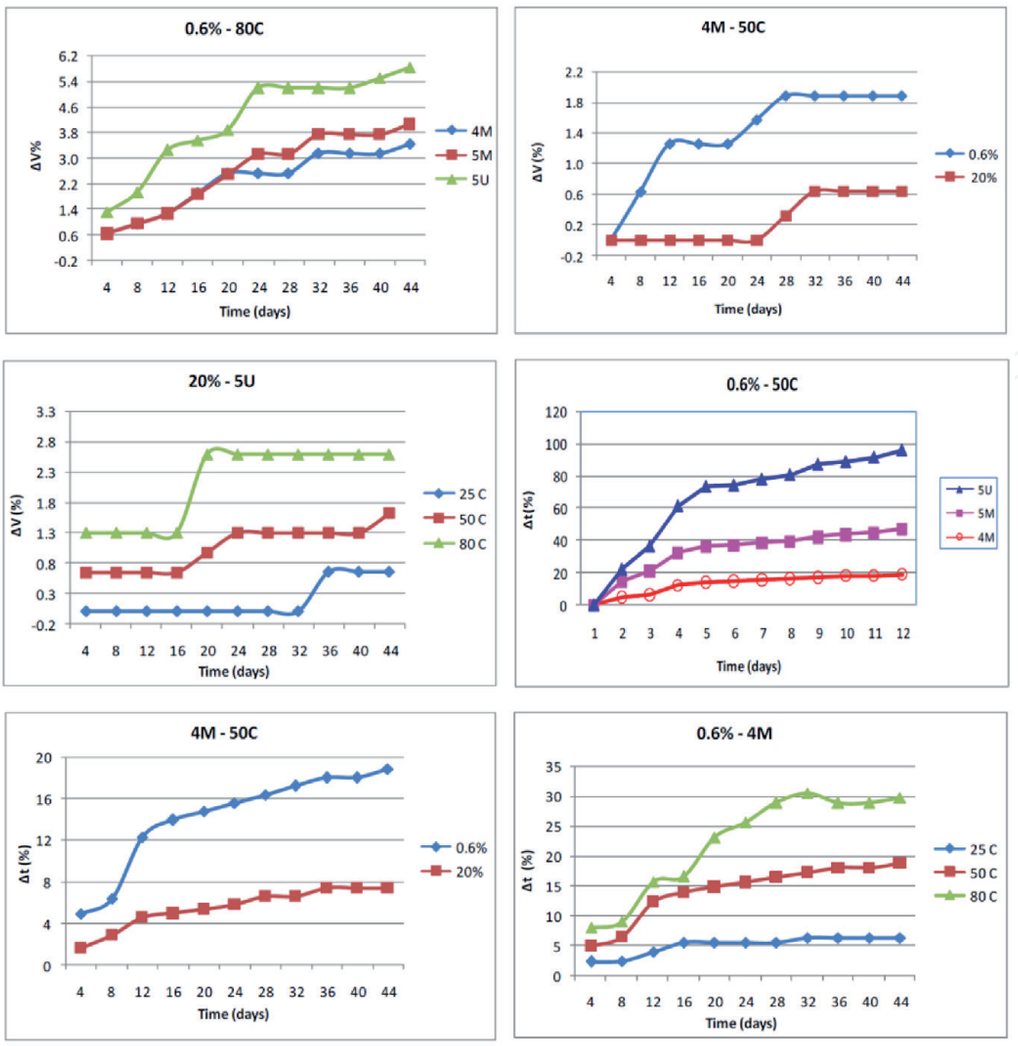

Figure 11.
Volume swelling of different sample configurations in 0.6% brine at 80°C (top left), of 4 M samples at 50°C in different salinities (top right), and of 5 U samples in 20% salinity at different temperatures (middle left). Thickness swelling of various sample geometries in 0.6% brine at 50°C (middle right), of 4 M samples at 50°C in various salinities (bottom left), and of 4 M samples in 0.6% salinity at various temperatures (bottom right).

4 M and 5 M curves. As discussed above, it is more probable that there will be larger amount of swelling (thickness change) for thicker samples, and for free (unconfined) samples as compared to the plate-mounted confined samples. When temperature and sample type are the same (eg. 4 M samples at 50°C; **Figure 11**), lower concentration (0.6%) solution yields larger thickness change. This is also natural and explained above; more swelling in dilute (less thick) solutions.

For the same salt concentration and sample configuration (eg. 4 M samples in 0.6% solution; **Figure 11**), we observe higher swelling curves for elevated temperatures, as expected. In one or two cases however, thickness seems to decrease with time. This may be some experimental error, as the general pattern is thickness increase with swelling time.

One important observation is that the total swelling amount (thickness or volume change) after the complete 45-day test period is surprisingly quite low. These samples were cut from swell packers used by the petroleum industry (elastomer sheets mounted on steel pipes). These packers were stocked in open yards for quite some time before being brought in for testing. It is well known that polymer properties are seriously affected by exposure to sun and moisture. This effect would be more prominent in the case of softer swelling elastomers. This will be discussed in more detail in Study-B.

Response of disc samples can serve as a reference, to assess the behavior of unconfined (free) elastomer. Plate samples represent the actual material response when elastomers sections are vulcanized onto steel pipes, and used as sealing elements in downhole applications. Similarly, volume swelling can be seen as a reference pattern for the swelling effect. In actual petroleum applications, thickness swelling is of actual interest as it directly relates to the sealing off of the gap between a tubular and a casing (or between a pipe and the rock formation).

3.3 Conclusions study-A

This study was primarily conducted to compare the material response of a swelling and an inert elastomer, both of EPDM type. Test plan and experimental strategy were carefully designed. Standard testing equipment was used for some of the tests, while test rigs and fixtures were designed and fabricated in-house for some other tests. All tests (except swelling behavior) were conducted in line with ASTM test standards. Inert elastomer EPDM2 was considerably harder than the swelling elastomer EPDM1 (in terms of shore-A hardness). As expected, compression set was higher for higher temperatures and longer testing times, more so for EPDM1 than for EPDM2. Room-temperature tensile set values were found to increase with testing time, again more noticeably for swelling (EPDM1) than for inert (EPDM2) elastomer. Tensile test data were converted into stress–strain graphs. Properties such as elastic modulus, tensile strength, and % elongation were extracted from the graphs. Values of fracture stress and percent elongation came out to be significantly lower for EPDM1.

Swelling tests were conducted on different sample types (unconfined and plate-mounted) for a total period of about 45 days, in brine solutions of different concentrations, and at different temperatures. In line with its inert nature, almost no swelling effect (volume or thickness change) was observed for EPDM2. For the swelling elastomer (EPDM1), volume and thickness swelling increase with increasing test temperature and decreasing salt concentration in a step-wise fluctuating fashion. Inert elastomer (EPDM2) is stronger than swelling elastomer (EPDM1), and one would assume that the sealing will last longer. However, in the case of water incursion, swelling elastomer will swell by a considerable amount, increasing the sealing pressure and providing a much better seal. All the applications of swellables in the petroleum industry (discussed in Chapter 2) are based on this novel swelling property of EDDM1 type of elastomers.

4. Study-B: Fresh vs. exposed elastomer

Zonal isolation packers and other forms of elastomer-mounted tubulars are often stacked in open yards for a long time before their deployment in wells. Elastomer properties may significantly change due to exposure (to air, sunlight, and humidity). Elastomer segments are generally covered by protective sheets; however, this wrapping can be damaged in places, exposing the elastomer to air, moisture and sunlight for long durations [8]. Some results from a comparative study of the behavior of fresh and exposed samples of an EPDM-type water-swelling elastomer are reported in this chapter.

Exposed elastomer material was provided by a local petroleum development firm, already mounted on steel pipes, ready for use as a swelling packer. Samples of fresh elastomer were supplied by a rubber development company working closely with the oilfield industry. Exposed samples are identified as EPDM1 while fresh

samples are labeled as EPDM2. Chemical composition of the elastomer cannot be disclosed due to proprietary rights.

4.1 Experimental work

Elastomer properties investigated are hardness, compression set, tensile set, tensile properties, and swelling behavior. To allow for a reasonably long swelling period, the swelling test was carried out for 1,000 hours (roughly 45 days). For tensile set, test durations of 10 min, 10 hours and 20 hours were used. Compression set test was conducted for 22-hour and 70-hour periods. Test procedures and methodology has been described in detail in Section 3.1 above.

Test conditions were carefully chosen to reflect actual well environment in shallow aquifers and slightly deeper wells in regional oilfields: three temperatures (room/ambient, 50°C, and 80°C), and two salt concentrations representing low and high salinities (6,000 ppm or 0.6%; and 200,000 ppm or 20%). Two sample geometries were used for the swelling test: disc samples (25 mm diameter, 6 mm thickness), and plate samples (elastomer vulcanized on 25 mm × 25 mm steel plates). Tensile set and tensile properties tests required ring samples (3 mm thickness, 1.5 mm radial width, inside and outside diameters of 16 mm and 19 mm). Disc samples were used for compression set and hardness tests.

4.2 Results and discussion

4.2.1 Hardness

Average hardness value for the exposed elastomer (EPDM1) was 51.3 on the Shore-A scale, while that for fresh samples (EPDM2) was 57.3. This is a significant difference, indicating that hardness of a water-swelling elastomer would increase by exposure to the elements. Increased hardness (or loss of flexibility) should generally result in lower amounts of swelling. Later results corroborate this conclusion.

4.2.2 Compression set

Plots of compression set CS (%) against temperature are shown in **Figure 12** for the two test durations of 22 hr. and 70 hr. As expected, compression set increases with temperature, the increase being sharper at higher temperatures. Also, as expected, CS curve for the longer test duration is higher than that for the shorter one. This means that if the elastomer is compressed for a longer time, or at a higher temperature (or both), the amount of permanent set would be larger. As far as the comparison goes, CS values for EPDM1 are much higher than those for EPDM2. This implies that the elastomer loses elasticity due to exposure (also indicated by the hardness results), producing higher permanent set due to compression, or relative lack of springback after the release of compressive force.

4.2.3 Tensile set

Standard test duration for tensile set (TS %) test recommended by ASTM is 10 min. However, 10 hr. and 20 hr. tests were added for comparison with material data available at some of the rubber manufacturers' sites, and to study the variation pattern more thoroughly. As shown in **Figure 13**, room-temperature TS increases with increasing test period. For the 10-min test, exposed and fresh samples yield almost the same TS value. For longer testing times, curve for EPDM1 is higher than

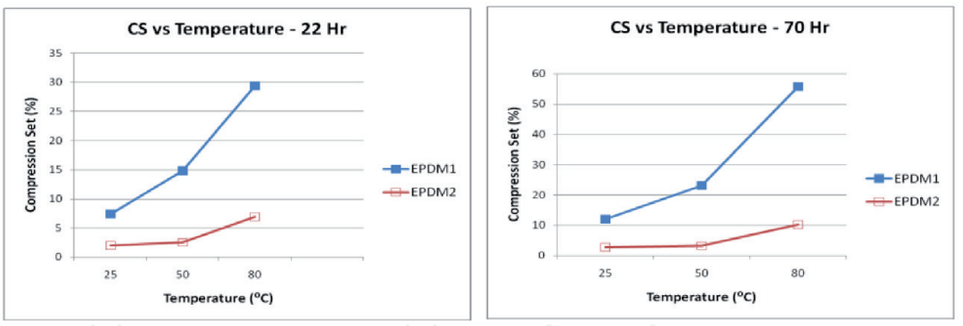

Figure 12.
Variation of compression-set with testing time and temperature.

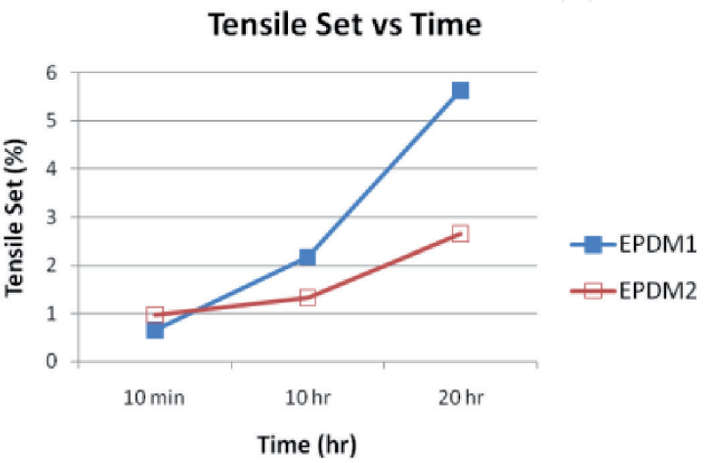

Figure 13.
Variation of room-temperature tensile set with testing time.

EPDM2, and increase in TS with time is also sharper for EPDM1. Higher permanent set under tensile loading again indicates loss of elastic recovery due to exposure.

4.2.4 Tensile properties

Figure 14 presents results of the tensile properties test for the two elastomers in the form of stress–strain graphs. As pointed out in Study-A, it is rather surprising to see that the entire stress–strain curve is almost linear for both EPDM1 and EPDM2. This would imply that the special filler materials and cross-linking used to produce swelling elastomers make them behave differently under tension as compared to normal elastomers. The fact that curves for the three samples of each elastomer are almost identical, together with the near-linearity of the curves makes it very convenient to calculate tensile properties, especially the elastic modulus (slope).

As summarized in **Table 1**, average fracture stress and elastic modulus for exposed samples are significantly higher than that for fresh ones. Percent elongation shows an opposite trend. This reinforces the previous results; exposure reduces the softness of the elastomer, resulting in lower flexibility (percent elongation) and higher fracture stress.

4.2.5 Swelling behavior

Being a water-swelling elastomer, the most crucial test was the determination of swelling response when the elastomer is immersed in saline water at different temperatures. In **Figures 15–18**, amount of swelling (volume change ΔV % and

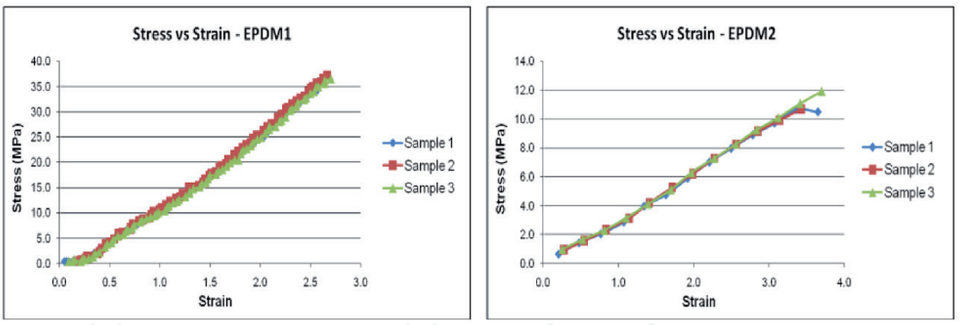

Figure 14.
Stress–strain plots from tensile test of three samples of fresh and exposed elastomer before swelling.

Elastomer type	Fracture stress (MPa)	Percent elongation (%)	Elastic modulus (MPa)
EPDM1 (Exposed)	35.96	264.47	14.40
EPDM2 (Fresh)	11.09	359.23	3.22

Table 1.
Average tensile properties of exposed and fresh elastomer.

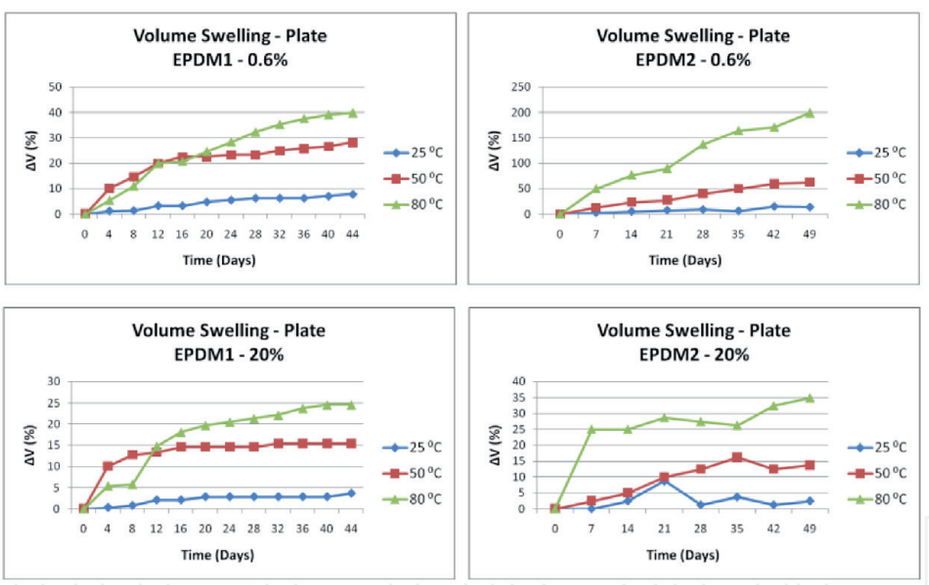

Figure 15.
Volume swelling of plate samples; low and high salinities; different temperatures.

thickness change Δt %) is plotted against time for different sample types and test conditions.

4.2.5.1 Plate samples

Figures 15 and **16** show the variation of swelling with time for plate samples. It is clear from all of the graphs that more swelling occurs when samples are kept under water for longer duration, as expected. As observed in Study-A, this increase in volume (or thickness) with time does not progress smoothly, but happens in a fluctuating manner. Swelling increases, then remains constant for some time, then increases again, and even decreases a bit at times. Possible reasons (buildup/reduction of salt content, and changes in cross-link structure) are the same.

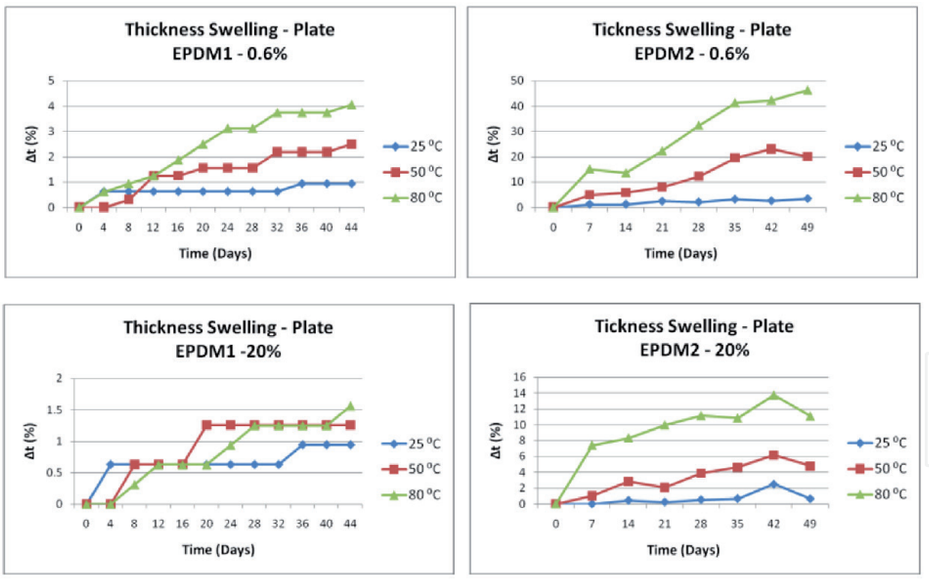

Figure 16.
Thickness swelling of plate samples; low and high salinities; different temperatures.

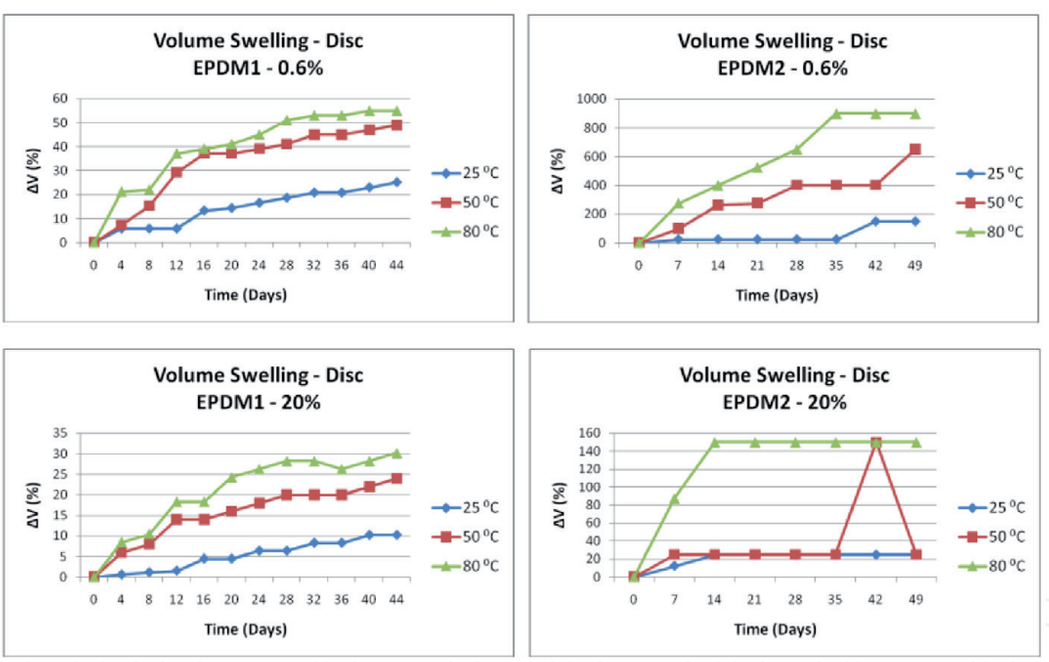

Figure 17.
Volume swelling of disc samples; low and high salinities; different temperatures.

Maximum swelling (volume or thickness) occurs for both elastomer types at a temperature of 80°C and under 0.6% salt concentration. Obviously, like most of the other materials, elastomers expand more with increasing temperature. Expanded pores allow more water to soak into the material, resulting in higher swelling. It is also natural that an elastomer would swell more in diluted solutions than in higher-concentration solutions, whether swelling happens due to diffusion or due to osmosis.

Volume swelling percentage is evidently much higher than thickness swelling; thickness change represents swelling in only one direction, while volume change corresponds to swelling from all exposed surfaces. Under the same conditions of salt concentration and temperature, fresh samples show substantially higher swelling than exposed ones (200% volume change compared to only 40% for 0.6%-80°C

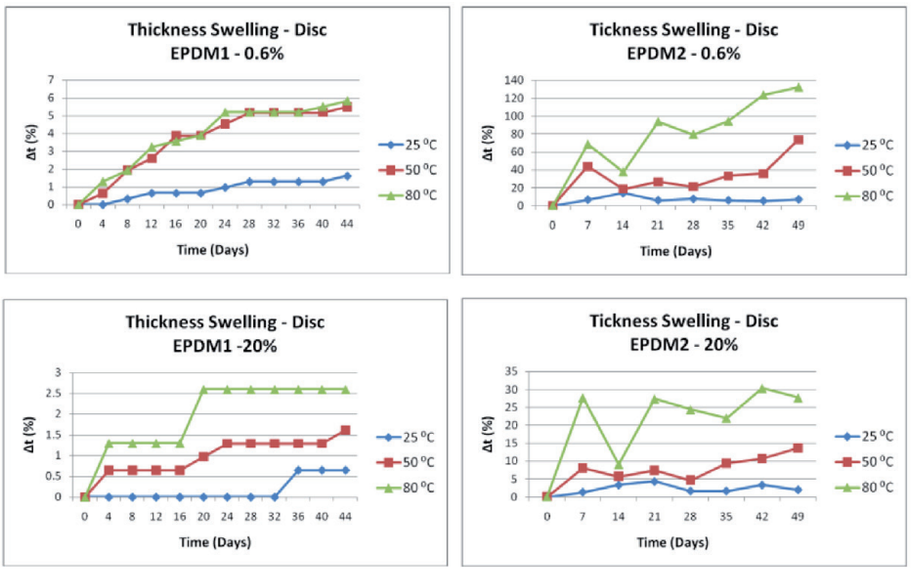

Figure 18.
Thickness swelling of disc samples; low and high salinities; different temperatures.

condition, for instance). This is in line with all earlier observations; extended exposure to sun, wind and moisture reduces elastomer flexibility and increases its hardness; harder and less elastic material naturally exhibits reduced amounts of swelling.

4.2.5.2 Disc samples

Volume and thickness swelling of disc samples is plotted against swelling-time in **Figures 17** and **18**. Like plate samples, discs also demonstrate the fluctuating swelling pattern. Also, in a similar manner, maximum swelling is observed at the highest temperature and the lowest salt concentration. As before, amount of volume swelling is far higher than thickness swelling. Most importantly, once again, fresh samples undergo noticeably higher swelling than exposed ones (900% volume change compared to only 55% under the 0.6%-80°C condition). Reasons for these observations for disc samples are the same as those described above for plate samples.

If we compare the swelling response of disc samples against plate samples, we notice a huge difference (for example, 900% volume change as against 200%, or 130% thickness change in comparison with 48%, under the same salinity and temperature conditions of 0.6% and 80°C). As explained earlier, disc samples are free to swell from all sides, while swelling of plate samples is restricted from one major surface; thus the sizeable difference.

4.3 Conclusions study-B

Comparison between material response of two sample sets of an EPDM-type water-swelling elastomer has been carried out through material characterization experiments, in particular the study of swelling behavior. One set of samples was cut from fresh elastomer, and the other from elastomer exposed to air, moisture, and sunlight. Shore-A hardness of exposed elastomer samples (EPDM1) was notably higher than that of fresh samples (EPDM2), indicating loss of flexibility with exposure. Compression set was found to increase with increasing temperature and testing time, CS values of exposed samples being significantly higher than fresh ones. Room-temperature tensile set values of the two sample types were almost the same for short-duration test (10 min), but were considerably higher for exposed

elastomer after longer-duration tests. Both compression set and tensile set values suggest that permanent set (or lack of springback) increases with exposure to the elements. Tensile properties test data surprisingly yielded almost linear stress–strain graphs for both sample sets, as against highly nonlinear graphs for most rubber-like materials. Average values of fracture stress and elastic modulus for the exposed elastomer were clearly higher, while percent elongation was lower, again implying that exposure reduces softness and flexibility of the elastomer. Rather than increasing steadily with time, swelling response showed a fluctuating trend for both elastomers. Higher amount of swelling is generally observed for higher temperatures and lower salt concentrations. Under the same conditions of temperature and salinity, fresh elastomer samples exhibited far more swelling (percent volume or thickness change) than the exposed samples. This strengthens the observation that elastomers lose suppleness if exposed to sun and moisture, etc. for extended periods of time.

5. Study-C: Swelling under water, oil, and acid

Well stimulation is the name given to techniques that are performed to increase or restore production. If a well initially exhibits low permeability, stimulation is used to start production from the reservoir. In other cases, stimulation is used to improve permeability and flow from an already existing well that has become under-productive. Acid induction, or acidizing, is used to either stimulate a well to improve flow or to remove damage. In matrix acidizing, acid is injected into the well, penetrating the rock pores at pressures below fracture pressure. The acid dissolves the sediments and mud solids within the pores that are inhibiting the permeability of the rock, thereby enlarging the natural pores of the reservoir and stimulating the flow of hydrocarbons, but this acid does not react with the hydrocarbons [9, 10].

Swelling beahavior of inert and swelling elastomers, and fresh and exposed elastomers was discussed in study-A and study-B above. Results from an experimental investigation are presented in this section about the behavior of two commercial elastomers, one water-swelling and one oil-swelling, with and without one-day acid exposure. Out of the one-month total testing time, one set of samples (for each elastomer type) was tested under acid for one day, and the other set without any acid exposure. Changes in volume swelling, thickness swelling, and hardness of elastomer samples were recorded at various prescribed times during a one-month swelling period. Selection of test parameters such as water salinity, temperature, acid concentration, and type of crude oil was based on actual field conditions in target regional oil wells.

5.1 Experimental work

Two sample geometries (disc and plate) were used for the two elastomer materials (one water-swelling, and one oil-swelling). All samples were provided by a regional oilfield operator, name and number of the elastomer not to be disclosed due to confidentiality reasons. Salt-water solutions of 35000 ppm (3.5%) and 85000 ppm (8.5%) strength were used to test the water-swelling elastomer, while crude oil from the field was used to swell the oil-based elastomer. The oil is classified as 'light crude oil, which is a liquid hydrocarbon that may contain up to 0.6 vol% benzene and other light aromatics and 0.8–1.5 wt% sulfur compounds, and has a viscosity of 200–450 cp. Same test temperature of 60°C was employed for both elastomers. To replicate conditions of acid induction in the actual wells,

samples were removed from water or oil after 3 days of swelling, and placed in 15% HCl solution for one day. They were then returned back to swell in water or oil. Measurements were taken on day-zero (no swelling) and after 1, 3, 4, 7, 15, and 31 days of swelling.

All reported results are average of readings from 3 samples; **Figure 19**. After measurements, plates and discs were returned back to their jars. In earlier studies, hardness samples were discarded after each measurement and were not placed back into brine or oil. There was a concern that small puncture marks made on the surface by the durometer indenter may affect future swelling to some degree. However, this necessitated a very large number of samples. For the current study, the rubber company opted for a limited number of samples, each one to be re-used after hardness measurements. This may result in minor deviations from expected swelling behavior.

5.2 Results and discussion

Results are presented in graphical format and behavior patterns are analyzed for swelling under water, under oil, and under water or oil with intermediate acid exposure for one day. Variations discussed are changes in volume and thickness swelling, and in hardness values. To have a general idea about the variation in data, all swelling related graphs include error bars based on a 95% confidence interval. Though results for all cases were carefully tabulated in detail and behavior patterns plotted, only a few are presented here for illustration. **Figure 20** shows physical exhibits of the amount of swelling (volume change, thickness change) and surface texture of swollen elastomer in some cases.

5.2.1 Volume change

Percentage change in volume due to swelling of disc samples against swelling time (number of days) in 35000 ppm and 85000 ppm brine solutions is shown **Figure 21**, with and without acid exposure. As expected, and as found in earlier studies [7, 8, 11], amount of swelling is higher in lower-strength brine than in higher higher-concentration one. Effect of acid exposure on swelling performance is not so straightforward. In 8.5% brine, swelling slows down during day-4 (when samples were removed from water and put into HCl solution), but does not do so in 3.5% salt solution. After this one-day acid induction, swelling amount steadily increases in both cases when the elastomer samples are placed back into the brine. Total acid-affected volume swelling at the end of the one-month period is almost the same

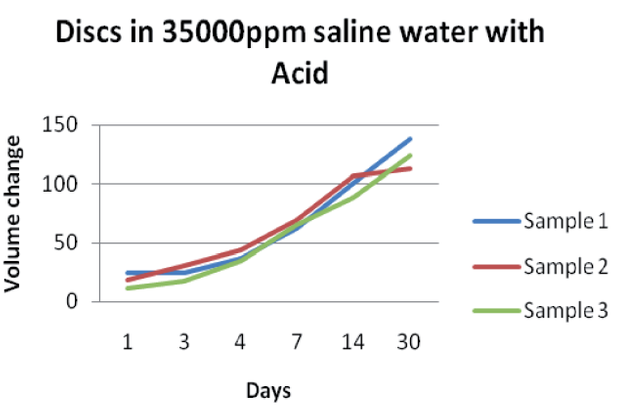

Figure 19.
A 3-sample graph of volume swelling against time for disc samples in 35000 ppm saline water.

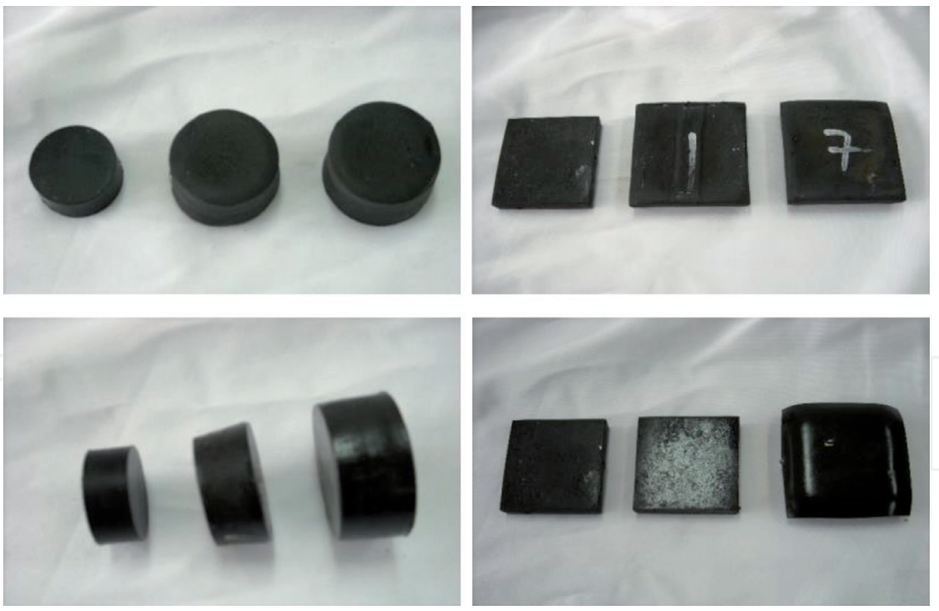

Figure 20.
Progressive swelling and surface texture of disc and plate samples in 35000 ppm saline water (above) and oil (below).

(with and without acid introduction) in 3.5% solution, but significantly higher in 8.5% solution. Plate samples of water-based elastomer exhibit similar behavior.

Volume change with swelling time for plate samples of the oil-based elastomer is shown in **Figure 21** (bottom). As for the water-swellable elastomer, samples keep up the swelling trend after the one-day acid exposure. Swelling goes down during acid-induction (day-4), but shows a somewhat erratic trend (increasing, decreasing, and increasing again) for the no-acid-exposure case. Total volume swelling after acid induction is significantly higher. Disc specimens also show similar swelling trend, though less irregular than plate samples. Higher amount of post-acid swelling for both water and oil-based elastomers hints at extra softening of the elastomer during acid exposure.

5.2.2 Thickness change

Variation of thickness for plate samples against swelling time (number of days) in 35000 ppm and 85000 ppm salt solutions is shown in **Figure 22**, with and without acid induction. As observed earlier, higher salt concentration leads to lower amount of thickness swelling. Total thickness change (one month swelling time) with acid exposure is a little higher in both cases. Change in thickness swelling against number of days for plate samples of the oil-swelling elastomer is shown in **Figure 22** (bottom). End-of-month thickness swelling is significantly higher in the case of acid exposure. Also, thickness swelling increases more rapidly after the one-day acid induction. Disc samples behave in a similar manner. Significantly higher amount of post-acid volume and thickness change indicates that there is more softening due to acid exposure in oil-swelling elastomer than in the water-swelling material. This observation is confirmed by the hardness results presented later.

5.2.2.1 Mechanism of swelling

Oil swelling elastomers are predominantly based on EPDM (ethylene propylene diene monomer, M-class) type of rubbers. Rubbers that have a saturated chain of the polymethylene type are categorized as M-class according to ASTM standard

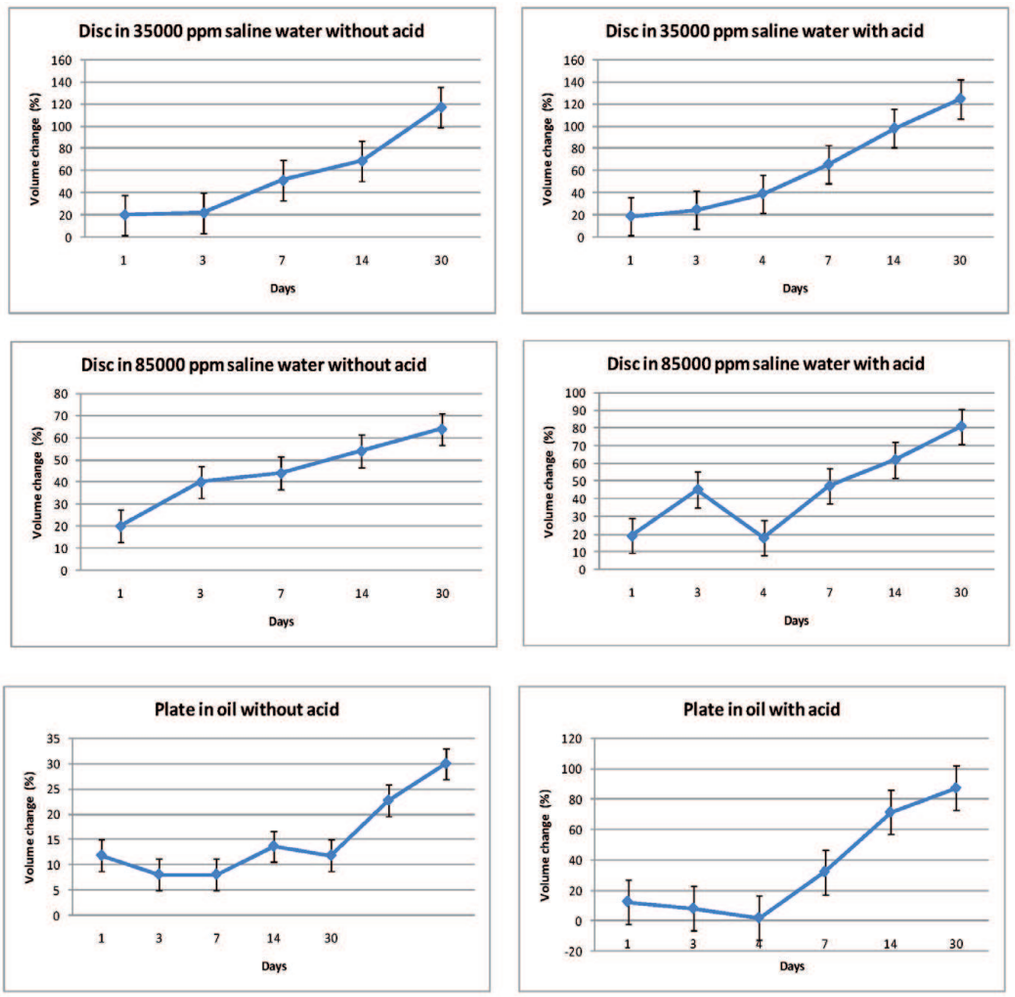

Figure 21.
Volume change (%) against swelling time, with and without acid exposure; disc samples in 3.5% and 8.5% brine solutions (top and middle); plate samples in oil (bottom).

D-1418. Materials with similar values of solubility parameter are likely to be miscible. Both EPDM and petroleum are nonpolar molecules, and are miscible together. It should be pointed out however that oil swelling in elastomers is not a process of dissolving the rubber. For instance, solubility parameter of diesel fuel is the 7.5–8.5 range, while that of EPDM is around 8.0 [12]. That is why uncured EPDM can be dissolved, while cured EPDM swells in crude oils. On the other hand, solubility parameter of NBR (nitrile-butadiene rubber) is about 9–10.5. Because of this significant dissimilarity, NBR swells very little in a hydrocarbon. Another important factor is the polymer-solvent interaction parameter [13] used by Flory and Huggins to represent the change of Gibbs free energy. Value of this interaction parameter for cross-linked EPDM and hydrocarbon is slightly greater than 0.5. EPDM type elastomers therefore swell rather than dissolve in crude oils. Interaction parameter value for oil swelling depends on various factors such as type of base elastomer, cross-linking density, type of oil, viscosity of oil, and operating temperature [14].

Water swelling elastomers are mainly compounded from nitrile or hydrogenated nitrile rubbers [15]. Super absorbent polymers (SAP), organic/inorganic salts, and/or any saline materials are a vital ingredient to boost the absorption of water into the rubber matrix to cause swelling. As an example, sodium polyacrylate is a polyelectrolyte SAP (widely used in disposable diapers) and swells due to osmotic pressure effects [16]. The anionic charge on the pendant groups of the polymer chain needs to be balanced by cationic counter ions (Na^+). To equalize the chemical potentials of the counter ions (or to maintain thermodynamic equilibrium), water

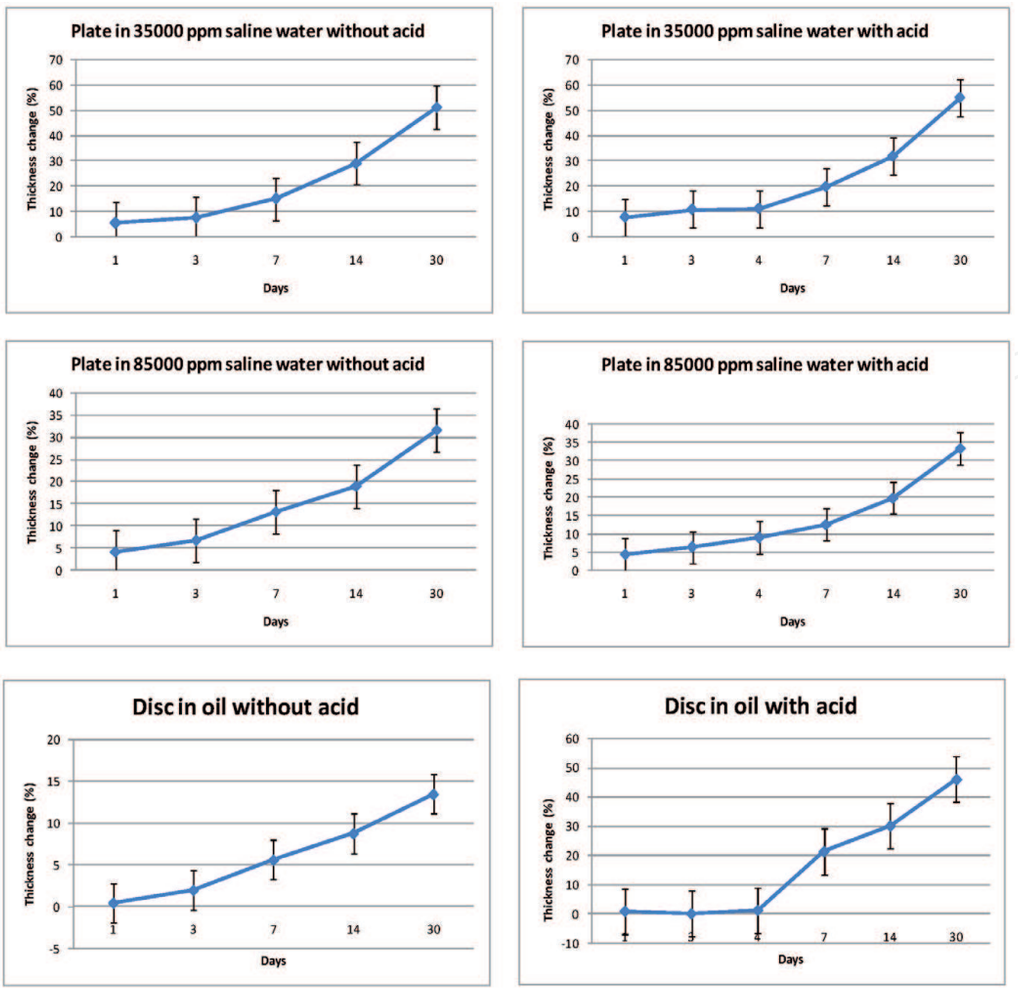

Figure 22.
Thickness change (%) against swelling time, with and without acid exposure; plate samples in 3.5% and 8.5% brine solution (top and middle); disc samples in oil (bottom).

migrates into the elastomeric matrix, leading to its swelling. The amount of swelling of the elastomeric matrix depends on the balance between the stretchability of the polymer network and the osmotic pressure effects of the counter ions. Elastomer stretchability is a function of cross-linking density, physical properties of the elastomer, and environmental temperature. Osmotic pressure depends on temperature, and the diffusion rate therefore increases with temperature, due to the higher movement of molecules in general [14].

5.2.3 Disc vs. plate samples

Amount of volume or thickness swelling for disc samples is significantly higher than that for plate samples in all cases (3.5% brine, 8.5% brine, oil), with and without acid exposure. This is both intuitively expected and borne out by earlier studies. Due to gluing/vulcanizing of the elastomer onto a metal base, plate samples are not free to swell on one major surface; disc samples have no such restrictions. Percentage change in swelling is therefore much lower for plate samples in comparison with disc samples.

5.2.4 Water-swelling vs. oil-swelling elastomer

Percent change in volume and thickness for water-swelling elastomer is generally far higher than that for oil-swelling elastomer. However, in one case,

oil-swelling elastomer shows an outlier behavior: higher volume swelling for disc in oil as compared to disc in water (for acid-affected samples). Field engineers can use this general trend to form an important operational policy: *to generate the desired sealing pressure, annular separation between the packer and the casing (or formation) for oil-swelling elastomers needs to be much smaller than that for water-swelling elastomers.*

5.2.4.1 Outlier behavior

The general pattern observed in all graphs is that swelling increases with longer exposure to the swelling medium, but the increase is not always uniform. This is in line with earlier works by the authors and by other researchers. However, in one or two instances (such as in **Figure 21**), swelling stops at a certain level, or goes down a bit, before increasing again. Water transport is a two-way mechanism; from the brine into the elastomer, and back from the swollen elastomer into the salt solution. In general, due to the prevalent concentration difference, there is a net movement of water into the elastomer, causing increase of swelling with longer exposure to water. Under certain conditions, and for brief intervals of time, the process can reverse (as in **Figure 21**), causing de-swelling of the elastomer. Very rarely, the contacting fluid might also leach out soluble constituents of the elastomer's recipe, to reduce test sample dimensions [17].

5.2.5 Hardness change

Reduction in hardness of an elastomer due to progressive swelling after prolonged exposure can significantly affect seal integrity. Variation in hardness against swelling time for disc samples in salt solutions of 3.5% and 8.5% concentration is plotted in **Figure 23**, with and without exposure to acid. Durometer hardness of original elastomer samples was around 53–55 on the Shore-A scale. Within 3 days of swelling, hardness sharply drops down to around 30, and then decreases more gradually with further swelling. Final hardness after one-month exposure is almost the same in both 3.5% and 8.5% brine, with and without acid induction. **Figure 23** (bottom) summarizes the hardness behavior against number of days of swelling for plate samples of oil-based elastomer. Hardness of the unswelled samples was about 58 Shore-A. In this case, it takes much longer for a significant decrease in hardness; one to two weeks of swelling. Also, acid injection reduces the hardness value significantly. Lower hardness values and larger amounts of volume and thickness change are consistent with each other. Acid exposure results in more softening of oil-based elastomer, which leads to higher amounts of swelling.

5.2.5.1 Drop in hardness and seal integrity

It can be easily observed that hardness behavior of both water-swelling and oil-swelling elastomers is quite similar, showing almost similar and significant hardness reduction the first few days (with and without acid). Large amount of swelling (as reported above for volume and thickness change) is good as it generates large sealing pressure. However, a practical question about long-term integrity is very important. How will the elastomer seal (with relatively soft swollen elastomer elements) perform over extended periods of time if subjected to high pressure differential? Reports from oilfields using swelling elastomer applications are encouraging in general. Enough sealing pressure is generated by the large amount of swelling to offset weakening of the material due to softening. Most of the applications work satisfactorily for at least a few years. However, it is rather impossible to arrive at

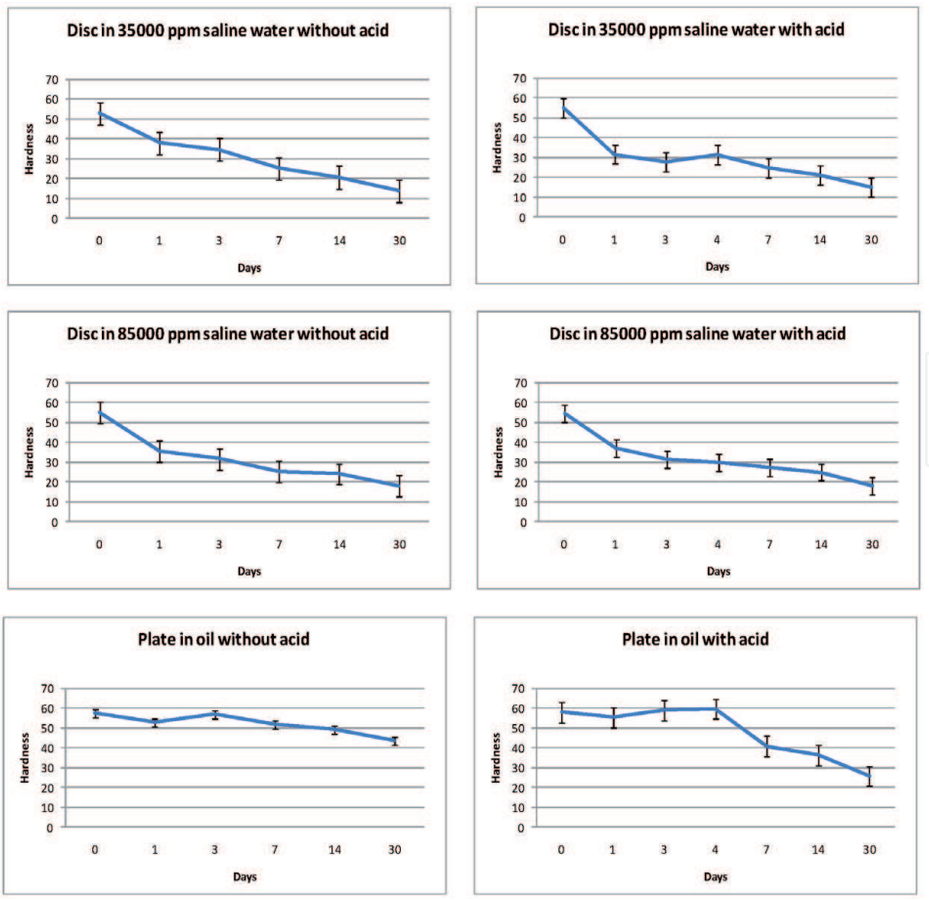

Figure 23.
Effect of swelling on hardness, with and without acid exposure; disc samples in 3.5% and 8.5% salt solutions (top and middle); plate samples in oil (bottom).

any reliable conclusion without actual long-duration tests under different conditions (temperature and pressure) and in different swelling media (saline water, oil, acid). An experimental facility for longevity testing of different water and oil-swelling elastomers has been designed and constructed by the authors at Sultan Qaboos University, Muscat, Oman [18]. Testing is in its fifth and final year by now. Conclusions from this one-of-a-kind ongoing study will be quite illuminating.

5.3 Conclusions study-C

A series of experiments was designed and carried out to investigate the effect of swelling on material response of a water-swelling and an oil-swelling elastomer, with and without acid exposure. Three swelling media were used: salt solutions of 35000 ppm and 85000 ppm concentration, crude oil, and 15% HCl. Testing temperature was 60°C in all cases. One set of elastomer samples (both water and oil-swelling) was placed into acid solution for one day after 3 days in the original medium (brine or oil), and was then put back into the same medium for the remainder of the one-month period. Measurements for volume, thickness, and hardness were done before swelling, and after 1, 3, 4, 7, 15, and 31 days of swelling. All readings were recorded for three samples and averaged out. As expected, lower concentration brine leads to higher amount of swelling. Being free to swell in all directions, changes in volume and thickness due to swelling are higher for disc samples as compared to plate samples, in water and in oil. For the one-day when samples are exposed to acid, amount of swelling generally goes down a little, before picking up again on exposure to the original media. Both elastomer types exhibit

a sharp decrease in hardness during the first few days of swelling, and then hardness gradually becomes stable for the rest of the swelling period. Acid exposure leads to higher amount of swelling and lower hardness values for both water and oil based elastomers during the remaining post-acid swelling time. Results from this investigation can be used by engineers and practitioners in oil and gas fields for pre-qualification and appropriate selection of swelling elastomers to suit targeted field conditions. These results can also be used as input parameters for modeling and simulation of swelling elastomer seal performance, leading to improvements in design and manufacturing of swell packers.

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