



Development of elastomers for oil, gas drilling uses

By Julien Ramier, John Staniland and Seth Hartshorne
Schlumberger Cambridge Research

Within the oil and gas industry, development of improved elastomer seals for surface and downhole hardware is critical for performance, reliability and safety reasons. Because of the downhole operating environment, elastomer seals are exposed to high levels of mechanical cyclic stress, high temperature and an aggressive chemical environment due to the nature of the drilling fluid used.

TECHNICAL NOTEBOOK

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To develop high-performance elastomers that satisfy these requirements, a novel experimental approach was designed based on a modified DMA system. Experiments were performed to investigate the mechanisms and the kinetics of elastomer degradation under more realistic drilling conditions than standard testing procedures. Variables investigated include dynamic deformation, frequency, temperature and chemical environment.

Based on the experimental data, the study focuses mainly on the interpretation of the output (elastic modulus) obtained by fitting data with a model, which enables deconvolution of the physical relaxation and chemical degradation processes. Understanding the impact of operational conditions on elastomer degradation in more detail will help developers produce robust materials and support predictive lifetime simulators.

Materials and methods

The material used for this study was an elastomer compound typically used in drilling applications. The base polymer was NBR with an ACN (acrylonitrile) content of 33 percent. A sulfur/EV (efficient vulcanization) curing system was used. N550 carbon black was added as the reinforcing filler to yield a hardness value of 70 Shore A.

The compound additionally comprised a standard package of additives, including plasticizers, antidegradants and processing aids. Following vulcanization, sample specimens were prepared with dimensions of 22mm (length), 6 mm (width) and a thickness varying between 0.5 to 2mm.

In terms of methods, degradation kinetics were measured using a DMA (Dynamic Mechanical Analyzer) with a

Executive summary

Operating in the downhole oil and gas environment exposes elastomers to extreme conditions, which leads to the progressive degradation of mechanical properties. This results in sub-optimal performance and, in some cases, premature failure.

A research and development project was initiated with the aim of developing high performance elastomers with increased fatigue-resistance, and thermal and chemical stability. The two-fold strategy comprised development of innovative tests to characterize mechano-physical degradation under environmental and cyclic fatigue conditions representative of the operating environment and development of new materials based on the knowledge acquired.

Significant progress has been made on understanding relevant chemical and physical processes that lead to elastomer failure under specific test-fluid and thermal conditions. The development of new protocols will enable more comprehensive elastomer-fluid compatibility analyses to be performed in the future.

In addition, the results of the study will contribute to the provision of optimized elastomer selection guidance and lifetime predictions for elastomers used in specific operational environments.

coupled pressure vessel, which enabled tests to be performed in fluid. Experiments were performed across a frequency (0.1 to 10Hz) and strain range (0 up to 20 percent). Tensile mode was used for this strain-controlled experiment.

Individual elastomer specimens were placed in the pressurized vessel and connected to the DMA. The aging fluid in the vessel was pressurized using either air or nitrogen (N₂) at a pressure of 9 bar, to prevent vaporization. The aging temperature ranged between 30 to 150°C.

In this study, deionized water was used as the aging fluid.

Results

A dynamic relaxation approach was used in which a constant deformation is imposed, and the resulting stress (or modulus) is recorded through the duration of the experiment. As shown in **Fig. 1a**, the elastic modulus is plotted versus time. The normalized modulus (right axis) also is used to compare the changes between varying experimental conditions.

The normalization shown in **Fig. 1b** is used to deconvolute the different contributions responsible for the changes. With this normalization, elastomer softening is displayed as an increase and hardening as a decrease.

The curves can be split in two regions as illustrated as 1 and 2 in both **Fig. 1a and 1b**. In region 1, a decrease (or increase) in elastic modulus is observed due to the softening of the materials, which results from the physical and chemical relaxation processes. In region 2, the increase (or decrease) in elastic modulus is a

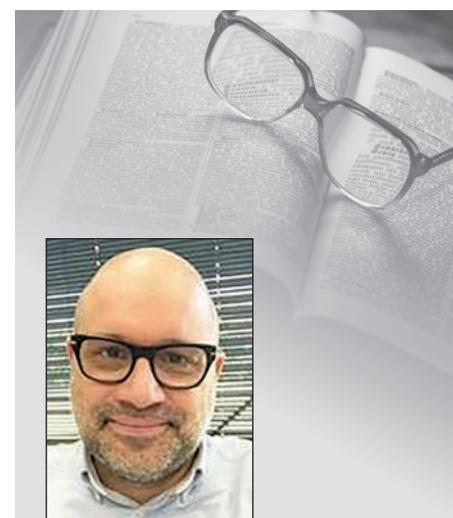
consequence of the hardening of the elastomer during the aging process.

Four types of experiments were performed in which the aging media, temperature and mechanical parameters (i.e. deformation, frequency) were varied. In the following section, interpretation of the response curves is explained by the deconvolution of the contributing factors.

Signal deconvolution

The dynamic relaxation signal shown in **Fig. 1b** can be deconvolved to show two phenomena, a physical relaxation and a chemical degradation.^{1,2} The physical relaxation (change in modulus) is affected by absorption of fluid and temperature.¹ The physical relaxation is associated with a reorientation of the molecular network, with disentanglement and rearrangement of chain entanglements and with the breaking of physical bonds (ie, vdW interactions) between polymer chains, the filler and polymer chains, and between filler particles (deagglomeration). These processes are initially rapid and decrease with time.¹

The chemical degradation process is indicated by two phenomena, softening induced by polymer intra-chain scission, and crosslink breakage and hardening, during which the normalized modulus reaches a maximum. The chemical degradation^{3,4} process occurs over a long duration (in these conditions above 24 hours) and predominates over the physical relaxation process. The chemical degradation process is sensitive to temperature as it is associated with chemical changes. These chemical changes



Ramier

The author

Julien Ramier obtained his doctorate in materials science from INSA de Lyon (France) for Rhodia (Solvay), working on the interface silica/elastomer and its impact on the Payne Effect and large deformations.

He joined Schlumberger in 2006 as a materials scientist focusing on product development for drilling applications. In 2013 he moved to Schlumberger Cambridge Research (U.K.). His current work focuses on the formulation and the development of advanced elastomer composites.

Ramier also is engaged in developing innovative characterization methods allowing the prediction of mechanical behavior and the lifetime of elastomer materials in extreme conditions. Over the last 20 years, his work has involved numerous collaborations with the main academic and industrial principals in the rubber industry.

are assumed to follow a simple first order Arrhenius relationship.⁵

Chemical degradation is strongly affected by the sample thickness, as it involves the diffusion of fluids or gas into and through the material. Hardening can result from the formation of additional crosslinks in a reactive elastomer (i.e. due to incomplete initial curing), but also the network chains see their flexibility affected.⁶ This is due to the appearance of bulky pendant groups resulting from thermal degradation and thermo-oxidation in the polymer chains, which can lead to a slight increase of the glass transition temperature.⁷ The hardening process is followed by the rupture of the specimen as the material becomes brittle.

The normalized modulus behavior can be described by the following equation:

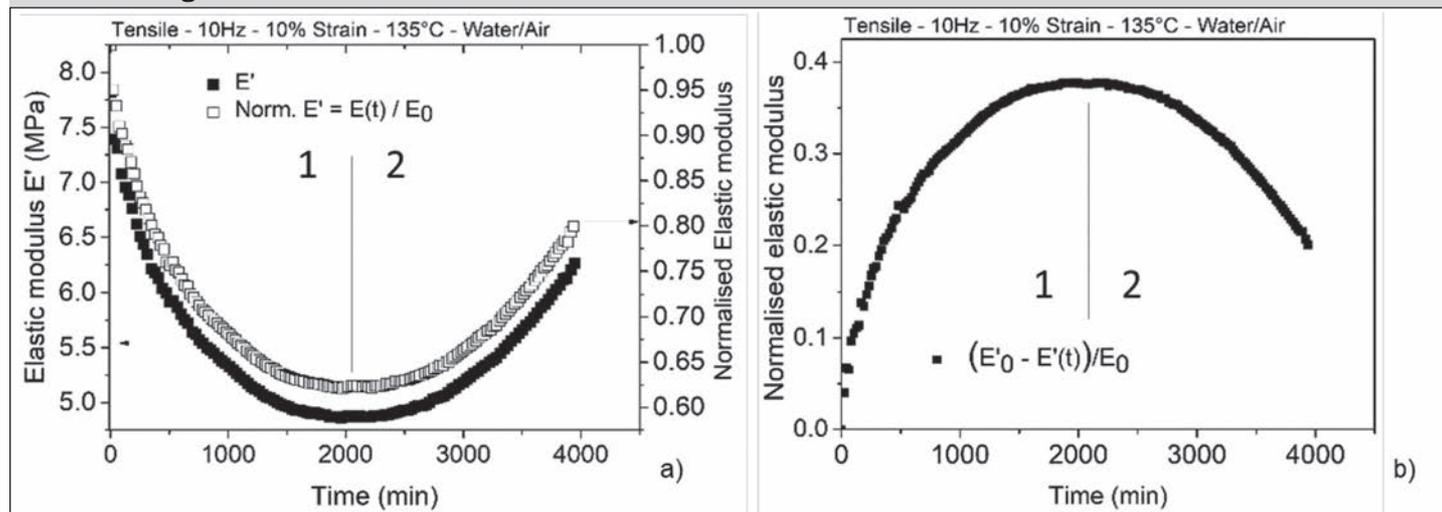
$$\frac{(E'_0 - E'(t))/E'_0}{g_{Soft}(t)} = A(T, media) * f_{Phy}(t) + B(T, media) * g_{Hard}(t) + C(T, Media) g_{Hard}(t)$$

where $f(t)$ describes the physical relaxation process and $g(t)$ the two chemical degradation processes.

The contribution of each of these events, A, B, C, can be estimated, and are shown to follow Arrhenius behavior.⁵ The relative activation energies and the dependence on other experimental parameters are discussed in the following sections. **Fig. 2** illustrates a representation of the model where each of the relative contributions are plotted versus the experimental data. The aim of this approach is to describe the aging behavior in realistic conditions and quantify their contributions to understand the weak points and predict the life of the materi-

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Fig. 1: Dynamic stress relaxation a) elastic modulus and normalized elastic modulus; and b) normalized in an alternative way to enable modeling of the curves.



Indiana man jailed for defrauding tire maker

By Jim Johnson

Rubber & Plastics News Staff

EVANSVILLE, IND.—An Indiana tire shop manager who claimed to have a handicap to avoid prison actually was trying to improve his handicap before heading behind bars.

And now fore actually means nearly four years in prison.

Joshua W. Eaden faces 46 months behind bars thanks to schemes he cooked up to defraud both a local business as well as tire maker Bridgestone Corp.

The 38-year-old Oakland City, Ind., man was a manager at Best-One Tire & Service in Princeton, Ind., when he defrauded Gibson County Coal through false invoices for foam tire fill services that never happened, according to U.S. Attorney Josh J. Minkler for the Southern District of Indiana.

Gibson County Coal paid more than \$189,000 in that scheme, the government said, and Eaden received higher bonus payments thanks to a higher net profit percentage at Best-One Tire & Service.

While Gibson County Coal was being billed for services not rendered, Eaden also reported phantom tire sales to Bridgestone to take advantage of a tire sales

rewards program that paid bonuses.

“Eaden reported tire sales to Bridgestone that never occurred and cited invoices related to the claimed sales that did not involve the actual sale of any eligible Bridgestone tires or substantially overstated the number and type of Bridgestone tires sold. As a result,

Eaden received bonuses as incentive rewards from Bridgestone for the fictitious tire sales,” the government said.

“Mr. Eaden was a trusted employee by many in and around the Princeton community,” Minkler said in a statement. “His greed got the best of him, and now his career of lies, deceit and fraud are over. This prosecution should remind those out there who defraud local businesses, that they will face real consequences.”

Best-One Tire & Service provided a variety of parts, supplies and services to Gibson County Coal, including industrial tires and foam tire fill, “a product made for inflating heavy equipment tires used in coal mining operations,” the attorney’s office said.

The fraud against both the tire maker and the coal company occurred between Nov. 1, 2013, and March 4, 2016, Minkler said.

Eaden actually was convicted last October on 17

counts of wire and mail fraud, but sentencing was delayed several times as he claimed he suffered a medical condition “severely damaged his vision and rendered him legally blind,” the government said.

When he showed up to be sentenced Sept. 2, 2020, he was wearing dark glasses and told a judge his vision was impaired. But the government countered that claim as an agent for the Federal Bureau of Investigation testified he saw Eaden playing golf and driving a golf cart during the time of his claimed disability.

“Golf course records reflected that Eaden had played golf constantly in 2020, including on days right after he asked the court to delay his sentencing because of his loss of vision,” the attorney’s office said.

The judge gave what the prosecutor termed an “enhanced” sentence of 46 months after reviewing the golf evidence, the attorney said.

“Mr. Eaden abused his position and the trust his company had in him for one simple reason—greed. To top that off, he thought he could play on the sympathy of the court for a lighter sentence by presenting a disability that was proven to be blatantly false through the dedicated work of our agents,” Paul Keenan, special agent in charge of the FBI office in Indianapolis, said in a statement.

Eaden, who has to pay a total of \$244,683 in restitution, also will be required to serve three years of supervised release after his sentence is completed.



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als under specific operational conditions.

In the following results section, all the curves are fitted using this approach and the dependence of A, B and C are estimated in relation to the operational parameters.

Effect of temperature on the aging process

Measurements were made across a temperature range spanning from 30°C to 150°C. The tensile deformation frequency was 10 Hz and the magnitude of strain (deformation) was 0 to 10 percent. Experiments were performed for a duration of 120 hours (7,200 minutes).

As shown in Fig. 1b, the curves show a softening response. In the first 10 hours (600 minutes), the softening rate increases with temperature. For temperatures below 80°C, the changes observed are below 15 percent compared to the initial state of the materials in these aging conditions, and the modulus stabilizes to a constant value. Above 80°C, up to 50 percent of the total change is observed after 50 hours (3,000 minutes) of aging.

At these temperatures, a change of slope is observable after longer times. Maxima are observed after 80 hours at

125°C, 40 hours at 135°C and 10 hours at 150°C. At temperatures above 100°C, all the specimens fractured within 120 hours.

After deconvolution, physical relaxation remains the most significant contribution. The chemical softening and chemical hardening provide a much lower contribution. The values of the three components, A, B and C, increase with temperature and follow Arrhenius behavior, showing a progressive increase in activation energy from A to C. The effect of temperature has a predictable and pronounced effect on the degradation kinetics with chemical degradation (polymer chain scission and re-crosslinking) predominating at temperatures above 100°C.

Impact of the aging media on the aging process: Pressurizing gas and the presence of oxygen

Experiments were performed using either air or nitrogen to pressurize the cell. The tests were performed at a temperature above 135°C, and at a cyclic deformation of 0 to 10 percent and a frequency of 10 Hz. At these temperatures, we observe a rapid increase corresponding to physical relaxation with no difference observed between the air or nitrogen environment, then a change of slope as the chemical degradation initiates. The slope is less pronounced in the pres-

ence of nitrogen. No clear maximum (before hardening) was observed in presence of nitrogen as the modulus tends to stabilize to a constant value.

A more accurate analysis using our deconvolution approach reveals no change in the physical relaxation between the sampled aged in either air or nitrogen. Both chemical degradation processes (softening and hardening) are significantly reduced in the presence of nitrogen.

This part of the study demonstrates the key impact of oxygen on the degradation process even when the material is immersed in fluid. Reducing the amount of oxygen helps to reduce both the softening due to chain scission and the hardening making the materials brittle. It is shown that controlling the oxygen level can allow elastomers to operate at higher temperatures for longer periods.

Impact of frequency on the aging process

Testing was performed in de-ionized water using compressed air at 150°C. Three logarithmically spaced cyclic deformation frequencies, 0.1, 1 and 10 Hz, were used. The magnitude of the strain was 0 to 10 percent.

Changing the frequency of deformation does little to change the normalized elastic modulus during the first 20 hours. Increased sample hardening is observed at 10 Hz after 20 hours when compared to the measurements at 1 and 0.1 Hz.

Analysis of the signal and the fitting of the curves shows no noticeable changes in terms of physical relaxation (A) and an increase for both chemical degradations (B and C) as the frequency increases.

Impact of deformation amplitude on the aging process

Specimens were tested in similar environmental conditions with air at 150°C. The cyclic deformation frequency was maintained at 10 Hz, and the deformation amplitude was performed at 5 and 20 percent.

The curves exhibit similar behavior in the first 10 hours, then the normalized modulus reaches a maximum before hardening is initiated. The major difference shown in these tests is the reduction in time taken before samples rupture, for example from about 40 hours at 5 percent to 20 hours at 20 percent.

Increasing the frequency and the deformation increases the degradation

rate by accelerating the chemical degradation process and reducing the time to the complete rupture of the specimen.

Conclusion

Whereas several studies have been performed on understanding the degradation of elastomer composites through monitoring the decline of the modulus, they generally only focus on the static behavior at low temperatures. This study highlights that it additionally is important to also consider the chemical hardening process.

At high temperatures all the degradation processes are accelerated and the lifetime above 80°C is considerably reduced. The interpretation of the curve presented in this work is a simplistic first attempt and currently is being improved.

In summary, the new experimental approach coupled with the interpretation approach enables us to select different formulations by comparing them and identify the specific impact of key additives when formulating a new material. It also helps to predict the lifetime of elastomers used for different applications.

An improvement in materials reliability also will come from the interaction between the materials designer and the fluids designer to develop optimal “system level” combinations of fluid/material to cover the wide range of elastomer applications across oil/gas operations.

References

1. C. Derham, *Plast, Rubber Compos. Process. Appl.*, p. 129, 1997.
2. K. Yamaguchi, A. Thomas and J. Busfield, “Stress relaxation, creep and set recovery of elastomers,” *International Journal of Non-Linear Mechanics*, vol. 68, pp. 66-70, 2015.
3. M. McKenna, “Response of Carbon Black Filler Butyl Rubber to Cyclic Loading,” *Rubber Chemistry and Technology*, vol. 54, no. 4, pp. 718-733, 1981.
4. L.A. Wood, et al, “Long-time creep in a pure gum rubber vulcanizate, influence of humidity and atmospheric oxygen,” *Journal of Research of the National Bureau of Standards, A Physics and Chemistry*, Vol. 78A No5, 1974.
5. J. Curro and E. Salazar, “Physical and Chemical Stress Relaxation of Elastomers,” *Journal of Applied Polymer Science*, Vol. 19, pp. 1,571-1,581, 1975.
6. J. Zhao, et al, “The effect of thermo-oxidation on the continuous stress relaxation behavior of nitrile rubber,” *Polymer Degradation and Stability*, pp. 32-37, 2015.
7. S. Kamaruddin, P.-Y. LeGac, Y. Marco and A. Muhr, 2011 in *constitutive Models for Rubber VII-Formation of crust on natural rubber after aging*, ed. Jerrams & Murphy, CRC press/Belkema, 2011.

Fig. 2: Deconvolution of the aging signal in the main contributions.

