Research Article

Guo Li*, Dasheng Zhu, Wenhua Jia, and Feng Zhang

Analysis of the aging mechanism and life evaluation of elastomers in simulated proton exchange membrane fuel cell environments

<https://doi.org/10.1515/epoly-2021-0078>

received June 17, 2021; accepted September 09, 2021

Abstract: This paper studies the aging mechanism of elastomeric gaskets made from silicone rubbers in simulated proton exchange membrane fuel cells (PEMFCs) in humid, acidic, and high-temperature environments. The changes in the surface morphology are observed using optical microscopy. Attenuated total reflection Fourier transform infrared spectroscopy (AFT-FTIR) and X-ray photoelectron spectroscopy (XPS) are used to investigate the changes in the chemical molecular structure. The stress relaxation test is conducted to characterize the decay process of the mechanical properties. The results indicate that cracks appear on the surface and that the aging mechanism is mainly due to decomposition in the backbone and hydrolysis of the crosslinking. The stress relaxation modulus decreases as the acid concentration increases, which suggests a decrease in elasticity and an increase in brittleness. A master curve that relates time and concentration is constructed. Based on this inference, the experimental time can be shortened by about four times.

Keywords: degradation mechanism, silicone, stress relaxation, fuel cell, lifetime

1 Introduction

Proton exchange membrane fuel cells (PEMFCs) are an alternative clean energy widely used in multiple applications, such as energy generation, transportation, and automotive industries, on account of their quick start, zero emissions, and high current density (1–3). Their long-term electrochemical performance limits widespread commercial use of PEMFCs. Therefore, most studies on PEMFCs investigate the overall performance of fuel cells, including the effect of components (4,5). In addition, gaskets between the bipolar plate and gas diffusion layers are employed to prevent leakage of reactant gases under the clamping load in the fuel cell. If the gasket materials degrade, the gasket will not only lose its sealing property, but also induce a mixture of hydrogen and air, which causes safety problems (6,7). Therefore, chemical stability and mechanical properties of gaskets are key issues in improving the performance of these fuel cells.

The gaskets in fuel cells are usually made from rubbers. These polymeric materials are subject to aging under all types of extreme environments, and their chemical and mechanical properties will change (8–10). These changes result in the failure of the entire component. Aging tests on gaskets have received significant attention because of gasket failures. Wu et al. (8) studied the effect of temperature on the mechanical properties of gaskets, including the tensile strength, elongation at failure, compression stress relaxation, and compression permanent deformation. The mechanical properties tend to decay as the temperature increases. Lou et al. (9,10) investigated the chemical structures and mechanical properties of nitrile rubber O-rings exposed to hydraulic oil and air. They found that chemical degradation is attributed to the loss of additives and oxidation reactions. The changes in mechanical properties, such as elongation at the breaking point, tensile strength, and Young's modulus, are due to the hardened brittle outer layer, voids, and agglomerates, which result in fracture morphologies. Bleszynski and Kumosa (11)

* **Corresponding author: Guo Li**, School of Mechanical Engineering, Nanjing Institute of Technology, No. 1 Hongjing Street, Nanjing, Jiangsu, 211167, China, e-mail: liguoperfect@163.com

Dasheng Zhu, Wenhua Jia: School of Mechanical Engineering, Nanjing Institute of Technology, No. 1 Hongjing Street, Nanjing, Jiangsu, 211167, China

Feng Zhang: School of Mechanical Engineering, Nanjing Institute of Technology, No. 1 Hongjing Street, Nanjing, Jiangsu, 211167, China; Nanjing Boiler and Pressure Vessel Inspection Institute, Nanjing, Jiangsu, 210002, China; Department of Mechanical Engineering, Nanjing Tech University, Nanjing, Jiangsu, 210009, China; Jiangsu Key Laboratory of Green Process Equipment, Changzhou University, Changzhou, Jiangsu 213159, China
ORCID: Guo Li 0000-0002-4972-2405

proposed a new model of silicone rubber exposed to electrolyzed aqueous salt. This model was verified by previous experiments. The polymer network exposed to electrolyzed aqueous salt was more significantly damaged than the samples exposed to non-electrolyzed standard aqueous salt conditions. The goal was to obtain the complex degradation mechanism in some critical lines and substations.

The accelerated durability test is an effective method for studying the degradation of polymeric materials due to the reduction of test time in the lab. Dubovský *et al.* (12) investigated the aging process and properties of gasket seal materials made of NBR exposed to critical operating conditions in aircraft engines. Static immersion tests in B10, B50, and B100 (representing 10%, 50%, and 100% biodiesel in diesel, respectively) were performed at 100°C for 500 h and at ambient temperature for 3,000 h. The aging behavior was described by calculating the relative changes of the physical properties, such as hardness and weight, and the trend of the mechanical properties, such as tensile strength and elongation. The surface morphology in the rubber was observed using optical microscopy and a camera. It was determined that either a higher temperature or a higher concentration of biodiesel can accelerate the degradation of the seals. Cai *et al.* (13) studied the aged biorejuvenated asphalts at a microscale and measured aging changes using FTIR, AFM, and component analysis. More special variations are appeared in the aged biorejuvenated asphalt. The Young's modulus changes significantly, indicating the degree of the aging. Tang *et al.* (14) studied the failure mechanism of NBR samples at room temperature for two years and aged mechanism using accelerated tests individually. The aging mechanism is different at 80°C due to free radical oxidation and at 90°C because of chain scission. The stress relaxation mechanisms are also different. Thus, the same aging mechanism is the foundation for accelerated durability testing in the lab. Recently, the aging process of seal materials used in PEMFCs has been attracting new focus (15–22). Pehlivan-Davis *et al.* (16) discussed the changes in properties and chemical structure of silicone rubber gasket seal material used in a fuel cell condition and an accelerated aging condition individually. The accelerated aging environments were made by sulfuric acid, and the test solutions had pH values of 1, 2, and 4 at elevated temperatures up to 140°C. The degradation mechanism for the samples in PEM fuel cell conditions was similar to the samples exposed to extreme conditions. Shen *et al.* (17) fabricated an EPDM with a multilayered structure. The hardness and the compression set increased as the layer number increased, which suggests a better sealing capacity.

The aging test was conducted, and it showed that the EPDM with a multilayered structure has better mechanical properties than did the blended EPDM. Tan *et al.* (7,21) and Li *et al.* (22) investigated the stability and durability of silicone rubbers and EPDM in PEMFC environments by detecting the chemical composition and recording the changes in the mechanical properties and conducting dynamic mechanical properties tests to analyze the aging process.

The goal of this study is to determine the chemical and mechanical degradation mechanisms of silicone rubber samples exposed to two solutions with different acid concentrations. The correlation between time and acid concentration is investigated to predict the lifetime.

First, optical microscopy is used to inspect the surface morphology of the materials. The absorbance of the chemical group is recorded using ATR-FTIR spectroscopy. The surface chemical composition and distribution of elements are investigated using X-ray photoelectron spectroscopy (XPS). Then, a stress relaxation test is performed to determine the mechanical aging process of the samples. A generalized Maxwell model is adopted to describe the stress relaxation behaviors, and the lifetime is predicted by constructing a relationship between time and acid concentration according to the principle of time-temperature superposition (TTS).

2 Experiments

2.1 Samples and experimental environments

In this study, silicone rubber, which is a commercial elastomeric material (Dongjue, Inc., China), was chosen for the tests. The material is crosslinked by polymethylsiloxane with vinyl and polymethylsiloxane with a hydrosilylated functional group. It is composed of siloxane by hydrosilylation, and the fillers are mostly composed of silica, quartz, and calcium carbonate. The silicone rubbers are shaped into squares (10 mm by 10 mm; 6 mm thick) and cylinders (12.5 mm in diameter; 6 mm thick). Two test solutions with different acid concentrations are prepared. One test solution is called the regular solution (RS). It approximates the actual PEMFC operating conditions (6,7,19,21). The solution includes 12.5 ppm sulfuric acid (H_2SO_4) and 1.8 ppm hydrofluoric acid (HF). The other solution, with $1 \text{ mol}\cdot\text{L}^{-1} \text{H}_2\text{SO}_4$, 30 ppm HF, is marked as ADT for the accelerated durability test in a short time. The aging temperature is controlled at 70°C.

2.2 Characterization methods

The samples were individually exposed to two different experimental conditions for a period of time. Then, the aged samples were taken out and cleaned before the tests. The modification of the surface morphology of the samples was analyzed using optical microscopy. The ATR-FTIR and XPS techniques can help qualitatively and quantitatively determine changes in the chemical structure. The ATR-FTIR was conducted to obtain the absorbance of the chemical group on the surface of specimens with the help of a Nexus Model 670 device, with a resolution of 0.1 cm^{-1} . XPS using a Thermo Fisher Scientific K-Alpha spectrometer with a monochromatic Al K α X-ray source was employed to analyze the chemical changes on the surface of specimens. The survey spectra ranged from 0 to 1,350 eV and were maintained at 1 eV steps for each specimen. The stress relaxation test was performed, and the compression Young's modulus was chosen to characterize the changes in the mechanical properties.

3 Results and discussion

3.1 Morphology analysis

The micro characteristic changes on the surface of the silicones are displayed in Figure 1. The magnification is 200 $\times$. Figure 1a and c show the micro topography of the unexposed samples. Figure 1b and d show the micro topography of the samples immersed into RS and ADT test solutions for 33 days at 70°C individually. It can be summarized from Figure 1 that the surface morphologies of the samples taken out of the RS test environment changed, but no cracks appeared (Figure 1c). The ADT test environment accelerates the aging of the samples from outside to inside. The surface becomes rough, and many cracks appear. The samples degrade severely in the ADT test solution. This aging process exhibits both acid-dependent and time-dependent processes. This conclusion is in agreement with the results found in previous research (7).

3.2 ATR-FTIR and XPS results

ATR-FTIR and XPS, advanced material analysis techniques, were chosen to investigate the chemical composition

changes on the surface of the silicone rubber specimens before and after aging under the experimental conditions. Figures 2 and 3 show the spectra of specimens measured using the ATR-FTIR method. The spectra ranging from 650 to $1,500\text{ cm}^{-1}$ are displayed in Figures 2a and 3a, and spectra from 2,500 to $3,500\text{ cm}^{-1}$ are displayed in Figures 2b and 3b. The spectra A in Figures 2 and 3 belong to the specimens before exposure. The spectra B in Figures 2 and 3 belong to the specimens after being immersed into two different solutions, respectively.

For unaged specimens (Figures 2a and 3a), the peak that appears at $1,412\text{ cm}^{-1}$ is ascribed to the rocking vibration of the CH_2 groups in the crosslinking area. The peak that appears at $1,257\text{ cm}^{-1}$ is caused by the $\text{Si}-\text{CH}_3$ bending vibration. A broadened peak from 1,057 to $1,007\text{ cm}^{-1}$ is strong and represents the characteristic of stretching vibrations of the backbone $\text{Si}-\text{O}-\text{Si}$. The peak that appears at 864 cm^{-1} is caused by the rocking vibration of the $\text{Si}-\text{CH}_3$ groups. A prominent peak near 785 cm^{-1} is ascribed to the coupling of the CH_3 chemical bonds rocking vibration and $\text{Si}-\text{C}$ stretching vibration. Two peaks that appear at 692 and $2,962\text{ cm}^{-1}$ are due to CH_3 chemical bond stretching vibrations. All these vibration modes at different spectra are analyzed based on prior references (7,23).

For specimens immersed in the RS test environment for 33 days (shown in Figure 2b), the intensity of all absorption peaks decreases compared with that of the unexposed specimens (Figure 2a). This phenomenon demonstrates that the chemical composition on the surface of the specimens changes after they are aged in the RS solution.

For specimens exposed to the ADT test solution for 33 days (Figure 3a), the intensity of the peaks weakens sharply with exposure time compared with that of the unexposed specimens (Figure 3b). The peaks at $2,962\text{ cm}^{-1}$ (CH_3) and 864 cm^{-1} ($\text{Si}-\text{CH}_3$) disappear for the specimen after 33 days of exposure. The intensities of the peaks at $1,257\text{ cm}^{-1}$ ($\text{Si}-\text{CH}_3$), 785 cm^{-1} (CH_3 , $\text{Si}-\text{C}$), and 692 cm^{-1} (CH_3) decrease dramatically. This may be due to the breakage of the side chain $\text{Si}-\text{CH}_3$. The peak at $1,412\text{ cm}^{-1}$ (CH_2) disappears after 33 days of exposure. This may be due to the hydrolysis of the crosslink point $-\text{CH}_2-\text{CH}_2-$ in the crosslink area. The intensity of the peak from 1,057 to $1,007\text{ cm}^{-1}$ decreases sharply, which suggests decomposition of the silicone rubber backbone $\text{Si}-\text{O}-\text{Si}$. Based on the comparison of the changes of peaks for specimens immersed in two different test solutions, the conclusion is that the degradation process of specimens is highly dependent on the concentration of the acid in the exposure environments. The solution with a higher acid concentration

Figure 1: Micromorphology of samples exposed to test solutions: (a) unexposed, (b) for 33 days-RS, (c) unexposed, and (d) for 33 days – ADT.

Figure 2: IR spectra for (A) unexposed specimens and (B) aged specimens in RS for 33 days at 70°C. (a) Wavenumbers from 650 to 1,500 cm^{-1} , and (b) wavenumbers from 2,500 to 3,500 cm^{-1} .

Figure 3: IR spectra for (A) unexposed specimens and (B) aged specimens in ADT solution for 33 days at 70°C. (a) Wavenumbers from 650 to 1,500 cm^{-1} and (b) wavenumbers from 2,500 to 3,500 cm^{-1} .

could make the Si–O–Si, $-\text{CH}_2-\text{CH}_2-$, and CH_3 structures decompose more seriously and accelerate the aging of silicone rubber materials.

For further analysis, the surface elemental compositions of specimens were determined using XPS. As shown in Figure 4a, survey XPS shows the presence of elements of silicon (Si), oxygen (O), and carbon (C) in the unexposed specimens. In addition, there is little fluorine (F). The high-resolution spectra for Si2p, O1s, and C1s (24–26), as shown in Figure 4b–d, respectively, in specimens before and after immersion into two different test solutions for 83 days are chosen to further study the chemical compositions. The high-resolution spectra for elements Si, O, and C are saved at each 0.1 eV step by deconvolution using curve-fitting. From Figure 4b–d, it can be seen that the binding energies of Si2p, O1s, and C1s for a specimen immersed in the RS test solution do not obviously change. For the specimens immersed in the ADT test solution, the binding energy (approximately 101.3 eV) of Si2p shifts 2 eV (Figure 4b) toward a higher binding energy level (approximately 103.2 eV). The binding energy of O1s (approximately

531.5 eV) shifts 0.9 eV (Figure 4c) toward a higher binding energy level (approximately 532.4 eV). The binding energy of C1s (approximately 283.75 eV) has no obvious shift.

Atomic concentrations of four types of elements are calculated by integrating the relevant peak intensities and are listed in Table 1. The proportion of C and Si atomic concentration (C/Si) and the proportion of O and Si atomic concentration (O/Si) for specimens over time are calculated and listed in Table 1. The atomic concentration ratio of C/Si decreases dramatically ($1.663 \rightarrow 1.556 \rightarrow 0.657$), while the atomic concentration ratio of O/Si increases ($0.919 \rightarrow 0.958 \rightarrow 1.416$) as the acid content increases in the solutions over time. The decrease in the C/Si atomic concentration ratio may be due to the hydrolysis of the crosslink bond $-\text{CH}_2-\text{CH}_2-$, which transforms it into Si–O under the action of the acid and temperature, and then it forms a different crystal structure SiO_2 from the original $-\text{Si}-\text{O}-\text{Si}-$ backbone structure. An increase in the O/Si atomic concentration ratio may occur because the side chain $\text{Si}-\text{CH}_3$ is transformed to Si–O under the action of oxidation and H^+ . First, the

Figure 4: XPS spectrum and high-resolution spectra analysis for the specimens: (a) XPS spectrum for unexposed specimens, (b) high-resolution spectra-Si2p, (c) high-resolution spectra-O1s, and (d) high-resolution spectra-C1s.

Table 1: Atomic concentration and ratios of atomic concentrations for specimens at 70°C

Samples	Atomic concentration (at%)				Ratios	
	Si	O	C	F	O/Si	C/Si
Unaged	27.74	25.49	46.13	0.64	0.919	1.663
83 days exposure in RS	28.28	27.10	44.01	0.6	0.958	1.556
83 days exposure in ADT	32.28	45.72	21.20	0.8	1.416	0.657

backbone Si–O–Si is transformed to an unstable Si–OH bond under the action of the acid, and then the Si–OH is transformed to a stable Si–O bond under the action of H^+ . In summary, these results may be due to the destruction of the $-CH_2-CH_2-$ and CH_3 chemical bonds. They may be oxidized and then transformed into Si–O bonds. Additionally, hydrolytic breakage of the backbone ($-Si-O-Si-$) may also lead to an increase in the O/Si ratio. The ATR-FTIR results are consistent with the XPS results.

Combining the ATR-FTIR and XPS analyses, it is determined that the changes in the chemical composition on the surface of the silicone rubber materials are caused by the decomposition of the main chain Si–O–Si in the backbone to form Si–O, the hydrolysis of crosslinks $-CH_2-CH_2-$, and the fracture of the side chain Si–CH₃ because of the oxidation and H^+ attack in the acidic experimental environments. A solution with a higher acid concentration causes more serious decomposition of the chemical structures and accelerates the aging of silicone rubbers.

3.3 Compression mechanical properties

Compression stress relaxation tests were performed on the silicone rubbers at 25% strain levels. The variations of the time-dependent Young's modulus are shown in Figure 5. The Young's modulus $E(t)$ increases more for the samples aged in the ADT test solution than the samples in the RS test solution and the unexposed samples, which represents a decrease in the elasticity. In general, the stress relaxation curves show a nearly exponential decay of stress with time. A higher acid concentration contributes to a greater increase in modulus and a faster decay of stress in the first, which indicates a poorer sealing property.

To better understand the viscoelastic behavior of the silicone rubbers, a generalized Maxwell model shown in

Figure 5: Stress relaxation modulus E versus time curves.

the Eq. 1 is adopted to describe the stress relaxation behavior of elastomeric materials. This model has multiple springs and dashpots. Because the components of the generalized Maxwell model are connected in parallel, all branches have the same strain at all times, and the overall stress of the system is the sum of the stresses in each branch (27,28):

$$\sigma(t) = \sigma_{\infty} + \sum_{i=1}^n \sigma_i e^{-t/\tau_i} \quad (1)$$

where σ_{∞} – stress after a long time, Pa; σ_i – stress, Pa; t – time, s; τ_i – a material constant, s.

The equation can also be rewritten as follows (Eq. 2):

$$E(t) = \frac{\sigma(t)}{\varepsilon_0} = \frac{1}{\varepsilon_0} \left[\sigma_{\infty} + \sum_{i=1}^n \sigma_i e^{-t/\tau_i} \right] = E_{\infty} + \sum_{i=1}^n E_i e^{-t/\tau_i} \quad (2)$$

where ε_0 – the strain.

When the Young's modulus is normalized, it becomes Eq. 3, which is called the Prony series:

$$g(t) = 1 - \sum_{i=1}^n g_i (1 - e^{-t/\tau_i}) \quad (3)$$

where $g(t) = \frac{E(t)}{E_0}$ and $g_i = \frac{E_i}{E_0}$.

The normalized stress relaxation modulus, called $g(t)$, versus time is shown in Figure 6. The curves displayed in Figure 6 show a similar trend. At the beginning, the modulus decreases sharply, indicating a quick relaxation of the stress. Afterwards, the modulus declines gradually over time. This test was stopped after 6 h due to the low relaxation rate. By comparing the two curves in Figure 6, it can be seen that the stress relaxes faster for samples from the ADT test solution than the samples from the RS test solution. Figure 6 shows the exponential decay nature of the stress with time similar to that described by

Figure 6: Normalized stress relaxation modulus for 2-week exposure samples at 70°C.

the Maxwell model. It also shows that a higher temperature contributes to a faster stress relaxation. Here, a method similar to the TTS principle, which represents the equivalence between time and temperature, is applied to study the viscoelasticity of the materials and predict the lifetime. The equivalence of time and acidic concentration are discussed and this method is named Time-Acid Superposition (TAS) principle. The mathematical expression is shown in Eq. 1. A master curve is constructed by shifting the curves a certain amount, α_T , horizontally to a particular reference test solution with acid concentration A_0 . Using the RS as the reference test solution, the curves of the samples in ADT solution with the acid concentration A are shifted to the reference test solution of RS in the logarithmic scale, as shown in Figure 7. The two curves overlap well. It can be seen that the time is longer than the actual experimental time. The stress relaxation master curve can

Figure 7: Master curve of stress relaxation for 2-week exposure samples at a reference solution of RS at 70°C.

Table 2: Fitted coefficients of the Prony series

g_1	g_2	g_3	τ_1 (s)	τ_2 (s)	τ_3 (s)
0.0421	0.0461	0.0243	18,492	37.8322	961.3681

be constructed using this principle of shifting to any reference test condition. The stress relaxation behavior for a long time period can be predicted in a short test time under a severe test condition by this method. The coefficients of the three-term Prony series have been fitted and listed in Table 2. In this experiment, the curve of samples exposed to the ADT test solution has been shifted by 0.898, fitted by the least square method, horizontally to the right on a logarithmic scale. The lifetime of the specimens is estimated to be about 27 h, while the test time under the ADT environment is only 6 h. The result points out that via the time-concentration superposition theory, the life extrapolating time is about 4 times of the experimental time at a harsh test environment. Cui et al. (26) studied the stress relaxation behavior of silicone rubbers aged in simulated PEM fuel cell environments and predicted a service life of approximately 6,000 h using the TTS principle. However, they also only studied the equivalence between time t and temperature T , without referring to the acid concentration. This work studied the equivalence between time and the acid concentration. The two curves overlap well via the time-concentration superposition principle. If the lifetime of seals compressed in a PEM fuel cell must be predicted, one can use the test data of the seals exposed to a severer test environment than its operating condition in a laboratory for a short time to construct the master curve. This is the advantage of equivalence between time and acid concentration. This work will provide a foundation for future studies, and this method will be investigated further.

$$E(A, t) = E(A_0, t/\alpha_T) \quad (4)$$

where $E(A, t)$ – stress relaxation modulus at time t and temperature T ; A_0, A – two different acid concentrations; t – time; α_T – shift factor.

4 Conclusion

In this work, silicone rubber, which is a potential gasket material, is aged in two test conditions prepared according to real PEMFC operational conditions. The degradation process is observed, and the degradation mechanisms are analyzed. The surface morphology of the samples

could range from smooth to rough, and cracks appeared during the aging process. The significant changes in the chemical structure of the specimens are mainly due to the decomposition of the backbone Si–O–Si, hydrolysis of the crosslinks $\text{–CH}_2\text{–CH}_2\text{–}$, and fracture of side chain $\text{–CH}_3\text{–}$. The chemical bonds are transformed into crystal structure SiO_2 . The stress relaxation modulus increases with the increase of acid concentration over time. This result indicates that the elastomeric material is losing its elasticity and the sealing force will decrease when the strain is held constant. The relation between time and concentration can be constructed to predict the lifetime of the material according to the TTS principle. The life extrapolating time is about 4 times of the experimental time at the environment with a higher acid concentration. This method could narrow the test time in the laboratory.

Funding information: This study is sponsored by the National Natural Science Foundation of China (51505212, 51505211, 11302097), Natural Science Foundation of Jiangsu Province (BK20201031), Scientific Research Fund for High-level Talents in Nanjing Institute of Technology (YKJ201952), Jiangsu Key Laboratory of Green Process Equipment (GPE202004).

Author contributions: Guo Li: writing – original draft, methodology, formal analysis; Dasheng Zhu: writing – review and editing, project administration; Wenhua Jia: investigation, funding acquisition; Feng Zhang: formal analysis, funding acquisition.

Conflict of interest: Authors state no conflict of interest.

References

- (1) Colak O, Acar A, Ergenekon E. Investigation of hygro-thermal cycle effects on the membranes of proton exchange membrane fuel cells. *J Test Eval.* 2014;42(2):285–90. doi: 10.1520/JTE20120201.
- (2) Xu LF, Fang C, Hu JM, Cheng SL, Li JQ, Ouyang MG, et al. Self-humidification of a polymer electrolyte membrane fuel cell system with cathodic exhaust gas recirculation. *J Electrochem Energy.* 2017;15:1–18. doi: 10.1115/1.4038628.
- (3) Zhao N, Xie Z, Shi Z. Understanding of nafion membrane additive behaviors in proton exchange membrane fuel cell conditioning. *J Electrochem Energy.* 2019;16:011011-1-5. doi: 10.1115/1.4040827.
- (4) Zhang YX, Li XG, Klinkova A. Numerical investigation of delamination onset and propagation in catalyst layers of PEM fuel cells under hygrothermal cycles. *Int J Hydrogen Energ.* 2020;46(19):11071–83. doi: 10.1016/j.ijhydene.2020.09.258.
- (5) Ghanbarian A, Kermani MJ. Enhancement of PEM fuel cell performance by flow channel indentation. *Energy Convers Manage.* 2016;110:356–66. doi: 10.1016/j.enconman.2015.12.036.
- (6) Li G, Tan JZ, Gong JM. Chemical aging of the silicone rubber in a simulated and three accelerated proton exchange membrane fuel cell environments. *J Power Sources.* 2012;217:175–83. doi: 10.1016/j.jpowsour.2012.05.105.
- (7) Tan JZ, Chao YJ, Yang M, Lee WK, Van Zee JW. Chemical and mechanical stability of a Silicone gasket material exposed to PEM fuel cell environment. *Int J Hydrogen Energ.* 2011;36(2):1846–52. doi: 10.1016/j.ijhydene.2009.12.048.
- (8) Wu Y, Wang D, Zhang W, Zhang J. Experimental research of thermal-oxidative aging on the mechanics of aero-NBR. *J Test Eval.* 2014;42(3):568–72. doi: 10.1520/JTE20130001.
- (9) Lou WT, Zhang WF, Wang HX, Jin TZ, Liu XR. Influence of hydraulic oil on degradation behavior of nitrile rubber O-rings at elevated temperature. *Eng Fail Anal.* 2018;92:1–11. doi: 10.1016/j.engfailanal.2018.05.006.
- (10) Zhang W, Lou W, Liu X, Xu D, Zhang J. The effect of accelerated aging on the properties of nitrile butadiene rubber (NBR) O-rings. *J Test Eval.* 2019;47(2):1533–50. doi: 10.1520/JTE20170265.
- (11) Bleszynski M, Kumosa M. Silicone rubber aging in electrolyzed aqueous salt environments. *Polym Degrad Stabil.* 2017;146:61–8. doi: 10.1016/j.polymdegradstab.2017.09.019.
- (12) Dubovský M, Božek M, Olšovský M. Degradation of aviation sealing materials in rapeseed biodiesel. *J Appl Polym Sci.* 2015;132(28):42254–1-7. doi: 10.1002/app.42254.
- (13) Cai LX, Zhang J, Gong M, Yang J, Chen X. Investigation of aging behavior of biorejuvenated asphalt with chemical and micro-mechanical methods. *J Test Eval.* 2018;47(5):3605–21. doi: 10.1520/JTE20170794.
- (14) Tang Q, He J, Fang X, Zhang W. Identification of failure mechanism consistency for NBR accelerated test. *J Test Eval.* 2016;44(1):47–54. doi: 10.1520/JTE20130252.
- (15) Ali S, Ghabchi R, Rani S, Zaman M. Characterization of effect of aging on polymer- and polyphosphoric acid-modified asphalt binders using X-ray diffraction (XRD). *J Test Eval.* 2020;48(6):4190–203. doi: 10.1520/JTE20180141.
- (16) Pehlivan-Davis S, Clarke J, Armour S. Comparison of accelerated aging of silicone rubber gasket material with aging in a fuel cell environment. *J Appl Polym Sci.* 2013;129(3):1446–54. doi: 10.1002/app.38837.
- (17) Shen LY, Xia LC, Han T, Wu H, Guo SY. Improvement of hardness and compression set properties of EPDM seals with alternating multilayered structure for PEM fuel cells. *Int J Hydrogen Energ.* 2016;41(48):23164–72. doi: 10.1016/j.ijhydene.2016.11.006.
- (18) Cui T, Chao YJ, Van Zee JW. Sealing force prediction of elastomeric seal material for PEM fuel cell under temperature cycling. *Int J Hydrogen Energ.* 2014;39(3):1430–8. doi: 10.1016/j.ijhydene.2013.10.086.
- (19) Li G, Tan JZ, Gong JM, Jia WH. Degradation mechanism of silicone rubber in simulated PEM fuel cell environment (in Chinese). *J Chem Indus Eng (China).* 2014;65:3669–75. doi: 10.3969/j.issn.0438-1157.2014.09.049.
- (20) Lin CW, Chien CH, Tan JZ, Chao YJ, Van Zee JW. Chemical degradation of five elastomeric seal materials in a simulated and an accelerated PEM fuel cell environment. *J Power*

- Sources. 2011;196(4):1955–66. doi: 10.1016/j.jpowsour.2010.10.012.
- (21) Tan JZ, Chao YJ, Wang HF, Gong JM, Van Zee JW. Chemical and mechanical stability of EPDM in a PEM fuel cell environment. *Polym Degrad Stabil.* 2009;94(11):2072–8. doi: 10.1016/j.polymdegradstab.2009.07.009.
- (22) Li G, Gong JM, Tan JZ, Zhu DS, Jia WH. Stress relaxation behavior and life prediction of gasket materials used in proton exchange membrane fuel cells. *J Cent South Univ.* 2019;26:623–31. doi: 10.1007/s11771-019-4033-72019.
- (23) Lin-Vien D, Colthup NB, Fateley WG, Grasselli JG. The handbook of infrared and raman characteristic frequencies of organic molecules. Boston: Academic Press; 1991.
- (24) Noll W. Chemistry and technology of silicone. Boston: Academic Press; 1968.
- (25) Yoshimura N, Kumagai S, Nishimura S. Electrical and environmental aging of silicone rubber used in outdoor insulation. *IEEE T Dielect El In.* 1999;6(5):632–50. doi: 10.1070-9878/99.
- (26) Delor-Jestin F, Tomer NS, Singh RP, Lacoste J. Characterization of poly dimethylsiloxane rubber upon photochemical, thermal, salt-fog ageings and exposure to acid vapours. *e-Polymers.* 2006;5:1–13. doi: 10.1515/epoly.2006.6.1.172.
- (27) Babaei B, Davarian A, Pryse KM, Elson EL, Genin GM. Efficient and optimized identification of generalized Maxwell viscoelastic relaxation spectra. *J Mech Behav Biomed.* 2016;55:32–41. doi: 10.1016/j.jmbbm.2015.10.008.
- (28) Cui T, Lin CW, Chien CH, Chao YJ, Van Zee JW. Service life prediction of seal in PEM fuel cells. *Exp Mech Emerg Energy Syst Mater.* 2011;5:25–32. doi: 10.1007/978-1-4419-9798-2_4.