8nd International Conference on Physical and Numerical Simulation of Materials Processing, ICPNS'16
Seattle Marriott Waterfront, Seattle, Washington, USA, October 14-17, 2016

Study on mechanical properties of silicone rubber materials used as gaskets in PEM fuel cell environment

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ABSTRACT

The gaskets made of silicone rubber materials are compressed in the PEM fuel cell to keep the gases and the oxidant in their own zones from leaking. The paper studies the mechanical properties of the silicone rubbers exposed to high temperature, humid air and acidic solution environment which is similar to the real PEM fuel cell operation condition. The compression set and stress relaxation tests are performed. The results indicate that the temperature, the humid air and the acidic solution have important effects on the mechanical properties of the silicone rubber materials. All the three factors can induce the increase of the stress relaxation modulus and the compression permanent deformation. This can accelerate the aging of the mechanical properties and decrease the sealing property of the gaskets which will influence the durability of the PEM fuel cell.
Keywords: mechanical properties; stress relaxation; compression; silicone rubber; PEM fuel cell

1. INTRODUCTION

The long term stability of proton exchange membrane fuel cell as a potential power source due to its high efficiency and zero pollution is critical. So the performance of the component at normal operation conditions in the PEM fuel cell is becoming a focus for researchers. The gaskets made of polymers are not only under a humid air, acidic solution, but also compressed in the fuel cell assembling by bolts to prevent form leaking[1-6]. The polymeric material knows to have viscoelastic property, i.e. the relationship between stress and strain strongly depends on time. If the strain is held constant, the viscoelastic will show "stress relaxation" behaviors. That is, the stress of materials decreased with time at a constant strain[7-9]. In sealing applications, stress relaxation of the gaskets after assembly directly reduced the sealing force. Then the gasket would lose its sealing capability when the stress in the gasket is lower than certain values.

Therefore, many researchers focus on the chemical degradation and the mechanical properties of silicone rubbers. Tan et al[2-4] have studied the chemical degradation and mechanical properties(dynamical mechanical property and hardness) of silicone rubbers and EPDM. Liu et al [10] have studied the nonlinear stress relaxation behavior of ductile polymer glasses from large extension and compression. The rate of the stress relaxation is found to be linearly proportional to the deformation rate for different polymer glasses. Huimin Li et al [11] have studied the effects of constructing different unit cells on predicting composite viscoelastic properties. Jiaohong Zhao et al[12] have studied the effect of the thermos-oxidation on the continuous stress relaxation behavior of nitrile rubber(125^{o}C, and 165^{o}C). And they found that stress increase ('rebound') after decay in air, but not in N_2. The chemical structure, crosslinking density and hardness investigations also investigated. Results indicate that at later stage thermos-oxidative crosslinking prevailed over chain scission causing stress rebound. The effect of atmosphere, temperature and original strain on the stress relaxation is also discussed. Vanessa A. Fernandes and Davide S.A. De Focatiis [13] studied the role of deformation history on stress relaxation and stress memory of filled rubber. Stress relaxation was found to be highly dependent on strain levels following a single loading.

Some researchers proposed an appropriate mode to fit the experimental data and predicted the service life of the materials. Such as, T. Rey et al[14] studied the influence of the temperature on the mechanical behavior(stress relaxation) of filled and unfilled silicone rubbers. The neo-hookean model was used to predict the experimental results previously presented. Anja Kömmling et al [15] studied the effect of heterogeneous aging in compressed HNBR and EPDM O-ring seals. Heterogeneous aging results in distorted bulk properties such as compression stress relaxation and compression set suggesting that HNBR has better performance than EPDM at 150^{o}C but which is not the case at 100^{o}C. Extrapolations of CS data are possible using time–temperature shifts and Arrhenius graphs. Exemplary CS values of 50% and 80% would be reached after approx. 10 years and 29 years, respectively for HNBR and after approx. 400 years and 1100 years, respectively for EPDM.

Tritala K. Vaidyanathan et al [16] have validated the predictive models of stress relaxation in selected dental polymers and obtained the predictive models by applying the master curves generated from short time experimental data by WLF time temperature superposition method. Hanna J. Maria et al[17] have found that the nature of nanoclay can influence the stress relaxation rate of the rubber/nitrile rubber nanocomposites. The organically modified clay could improve the mechanical property. And the Maxwell-Weichert model was proposed and well to fit the experimental values. Ken Yamaguchi et al [18] studied the stress relaxation, creep and set recovery of a cross-linked unfilled natural rubber in tension. A method based upon the Boltzmann superposition principle was used to compare the creep compliance with a measurement of its recovery after release from a range of constant loads held for different time. Cui et al[7-10] Have studied the mechanical properties of silicone rubber and EPDM in fuel cell environments and predicted the service life of by master curves and Maxwell model.

The present paper is concerned with the compression set and the compression stress relaxation behavior of the polymers in both ambient air and wet conditions, at strain levels of 25% and at elevated temperatures. This study is a foundation for providing experimental data for predicting the service life of the gaskets.

2. MATERIAL AND EXPERIMENTS

2.1 Material and preparation

Silicone rubber is a promising candidate for gaskets in PEM fuel cell. In general, silicone is able to be cross-linked using peroxides, and the popular fillers are carbon black and calcium carbonate. It has already been widely used as gaskets in other applications because of (due to) its flexibility and resistance to weathering. It is stable in temperature from -40^{o}C to 120^{o}C. Its glass transition temperature at -54^{o}C is relatively low and it can remain flexible, elastic, and retains its properties up to 150^{o}C[9]. Although its surface chemistry may change over time when exposed to PEM fuel cell environment, its bulk mechanical properties remain intact. However, like most polymers, silicone rubber also shows viscoelastic behavior especially at high temperature.

In this work, commercial silicone rubber in sheet form was obtained from the manufacturer in China and cut into round buttons for compression stress relaxation tests. In our experiment, A cylindrical disc with a 13 mm diameter(D) and 6.3 mm height(H) can be used for compression tests according to standard for convenience. It is worth noting that it is difficult to make the samples perfectly cylindrical if it was directly punched out from a sheet material. A tool was designed and used to cut the sample out from the sheet to make it as cylindrical as possible.

Three solutions were used to age the materials. The first solution just composed with reagent grade water having 18 Mega Ohm resistance. The second solution is termed a “Regular” solution(RS). Chemical composition of the solution is 12 ppm H_2SO_4, 1.8ppm HF with reagent grade water having 18 Mega Ohm resistances. The PH value is about 3~4. The third solution is an accelerated durability test(ADT) solution. The final composition is 1M H_2SO_4, 12 ppm HF and reagent grade water having 18 Mega Ohm resistances. The PH value is less than one. Besides, the unaged samples and the samples exposed to air under different temperatures were used to compare.

The cylindered-shaped specimens were prepared and exposed to different solutions individually. The aged samples were taken out of the test bottles at selected times for observation and test.

2.2 Instrument

The compression set and the stress relaxation tester made by Mingzhu, China, was used in this experiment. The particular mode consists of three independent testing rigs. Each can test the sample at a certain level 10%, 15% and 25%. The third level is chose in this paper. The sealing force can be recorded by a computer throughout the test period with time.

2.3 Experiments

The specimens shaped from silicone rubber materials were immersed in the air, in the DI water, in the RS and in the ADT environments at temperatures 30 °C, 70 °C and 90°C individually. Then the exposed samples were detached for compression set test and stress relaxation test at 25% strain levels individually at room temperature for every selected time.

The test procedure follows the GB/T 7759-1996 and GB/T 1685-2008, such as pre-conditioning of the test specimen and the 25% strain applied at the test temperature.

The data published in this studied can help understand the effect of different factors such as temperature and environmental exposure on the compression mechanical properties of gasket seals.

3. Result and discussion

3.1 Compression set

The samples immersed in DI water for different time were taken out for compression set test. The samples were sandwiched at 25% strain level for three days. Then the thickness of the samples were measured and compared to that of uncompressed samples. The deformation was calculated according to equation 1. The results are shown in Fig.1 to Fig.3.

$$C = \frac{H - H'}{H} \times 100\% \quad \text{(equ.1)}$$

C -the deformation rate

H' -the height of the sample after compression

H -the height of the sample before compression

Fig.1 shows the compression permanent deformation versus time curves obtained from strain levels at 25% for specimens in DI water at two temperatures, 30°C and 70°C. It can be seen that the compression permanent deformation increases with the exposure time of the samples in DI water. The trends of two curves are similarly to each other. But the deformation of samples exposed at 70°C is higher than that of samples exposed at 30°C for each same exposure time. The deformation reaches up to 5% when the exposure time over 100 days. The deformation rates are about 4.7% and 4.0% for samples exposed at 30°C and 70°C for 30 days individually. The larger deformation represents that the resilience of the silicone rubbers is getting worsen. However, the silicone rubber is used as gasket because of its hyperelasticity and viscoelasticity properties. So this result indicates that the mechanical property of the materials is deteriorated and the temperature plays an important role on the decay of the mechanical property.

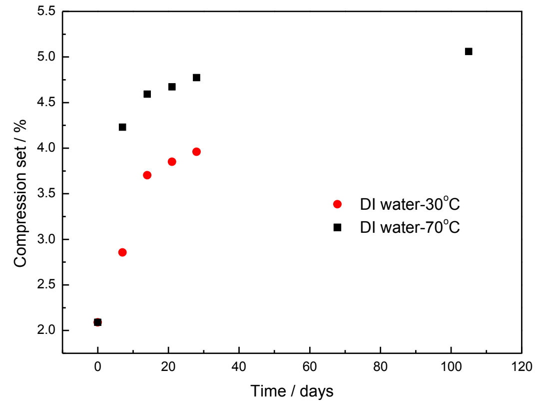

Figure 1 Compression set of silicone rubbers exposed to DI water at 30 °C and 70 °C

The effect of the exposure environment DI water on the deformation is shown in Fig.2. From the Fig.2, it can be seen that the trend of the curves just like that in Fig.1. The deformation of the samples in DI water is just a little larger than that of the samples in air. Compared with Fig.1, it can be observed that the DI water has an effect on the deformation but less than the temperature.

Fig.3 shows the compression permanent deformation versus time curves obtained from specimens exposed to DI water, regular solution(RS) and accelerate durability solution(ADT). From Fig.3 it can be seen that the deformation of samples in DI water is similar to that in RS. But the deformation of samples in ADT is larger than the two before. The

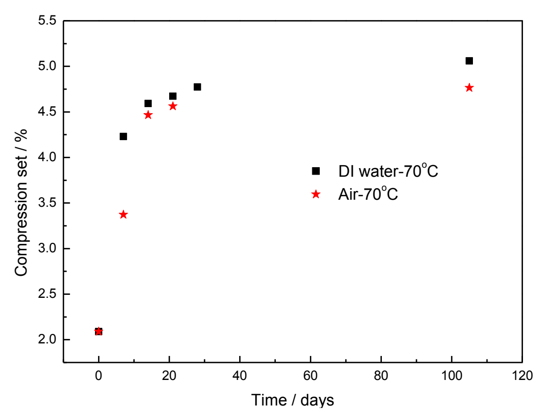

Figure 2 Compression set of aged silicone rubbers with or without DI water

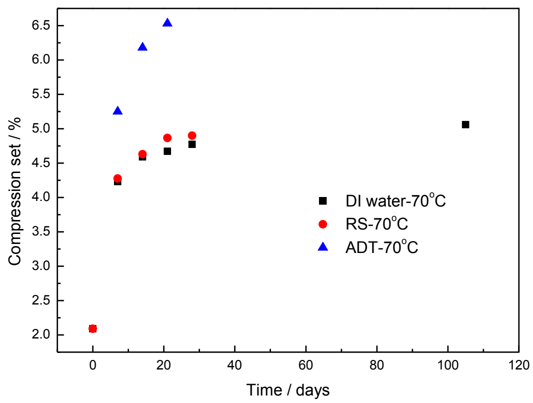

Figure 3 Compression set of aged silicone rubbers in different test solutions

deformation increases to 6.5% when the samples immersed to ADT solution for about 20 days while up to 5% for samples exposed to DI water for 100 days. The results indicate that the elastic property of the silicone rubber deteriorated most in the higher concentration acid solution.

3.2 Stress relaxation

The immersed samples were taken out for compression stress relaxation test. The test data was recorded by computer every second.

Fig.4 shows the stress relaxation curves(time dependent Young's modulus) obtained from strain levels at 25% for specimens in ambient air at three temperatures, 30°C, 70°C, and 90°C for 1 weeks. Although not perfect, the three curves are pretty close to each other. Besides, there is another curve of unexposed samples for compared. From this figure, it can be seen that the modulus E decreased dramatically at first. After 10,000s, it decreased steadily with time. The results indicate that the stress exponentially decays with time, which shows the stress relaxation behavior of the silicone rubbers.

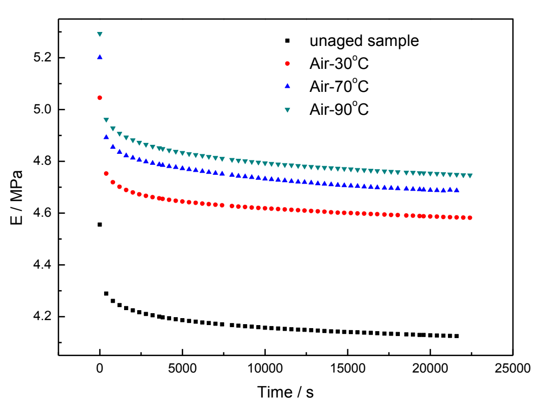

Figure 4 Time dependent compression stress relaxation modulus E of silicone rubber at three different temperature levels

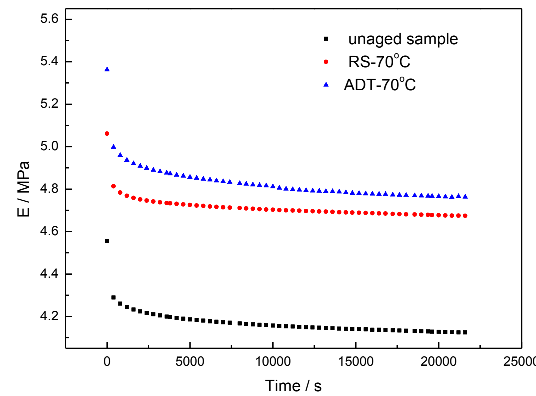

Figure 5 Time dependent compression stress relaxation modulus E of silicone rubber exposed to test solutions at the temperature of 70 °C

Besides, the Young' modulus represents the elasticity property of the materials. The higher modulus illustrates the increasing stiffness of the materials. That is to say the silicone rubber materials exposed to ambient air at 90°C loses its elastic property largely to some extent and the sealing property of gaskets made of silicone rubbers will be damaged. The experimental data was picked up before previous 6 hours, since the relaxation rate at this time is sufficiently low.

Fig.5 shows the time dependent Young's modulus curves at two exposure conditions, RS and ADT, at temperature 70°C with 25% applied strain. It can be seen that the Young' modulus increased with the increasing acid concentration in the exposure environment. The acid can affect the elastic property of the silicone rubbers. The mechanical property is getting worse in the highly acid environments. This result corresponds with the reference[8-9]. The acid solution could degrade the chemical properties, and also could degrade the mechanical properties.

Fig. 6 shows the time dependent Young's modulus curves for samples exposed to RS solutions at 70°C, but for different exposure time,1week, 2 weeks, 3 weeks, and 4 weeks. It can be observed that the exposure time can gradually affect the elasticity of the silicone rubbers. The sealing property is aging with time under PEM fuel cell. So the durability of gaskets is critical for PEM fuel cell.

In short, it can be seen that the temperature, the environment, in which the specimens are exposed to and the exposed time can affect the relaxation rate greatly. The water can also affect the chemical composition of the samples which can affect the mechanical behaviors, just like the acid solution. The exposed environments can attack the backbone of liquid silicone rubber and cause chain scission and higher temperature can accelerate this process[1].

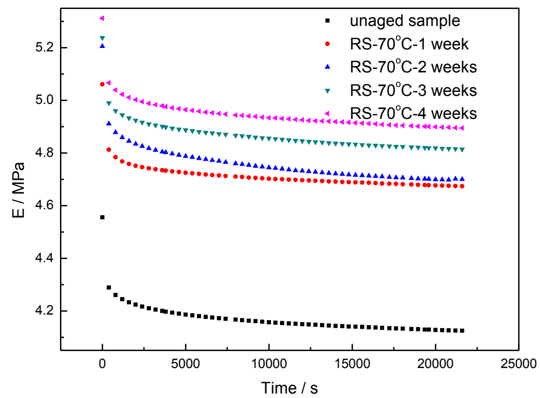

Figure 6 Time dependent compression stress relaxation modulus E of silicone rubber exposed to RS up to 4 weeks at the temperature of 70 °C

4. CONCLUSION

The paper presents experimental studies of compression set and stress relaxation behavior of silicone rubbers in ambient air, DI water and acid solutions at different temperatures, under applied 25% strain level. From the experimental data and analysis, it is concluded:

1. The factors including the temperature, the water and the acid, all can affect the mechanical properties, compression set and stress relaxation behavior greatly, especially the higher temperature and the higher acid solution.

2. The compression permanent deformation and the stress relaxation modulus E are increasing under the more harshly environments which indicate the decrease of the elasticity of the silicone rubbers.

3. The temperature and the exposure environments can damage the mechanical properties by increase the compression permanent deformation and Young's modulus, which indicates the bad re-bound and elasticity decreased.

5. ACKNOWLEDGMENTS

This study is sponsored by the National Natural Science Foundation of China(NO.51505212, NO.51505211, NO.11302097), Postdoctoral Science Foundation of Jiangsu Province of China (NO.1301060B), Natural Science Foundation of the Jiangsu Higher Education Institutions of China (NO.11KJD130001).

REFERENCES

Brew, D. R. M., & Glasser, F. P. (2005). Synthesis and characterisation of magnesium silicate hydrate gels. *Cement and Concrete Research, 35*(1), 85-98.

[1] Guo Li, Jinzhu Tan, Jianming Gong.Chemical aging of the silicone rubber in a simulated and three accelerated proton exchange membrane fuel cell environments[J].*Journal of Power Sources*. 217 (2012) 175-183.

[2] J. Tan, Y.J. Chao, M. Yang, W.K. Lee, J.W. Van Zee, *Int. J. Hydrogen Energy* 36(2011) 1846-1852.

[3] J. Tan, Y.J. Chao, J.W. Van Zee, W.K. Lee, *Mater. Sci. Eng. A* 496 (2008) 464-470.

[4] J. Tan, Y.J. Chao, M. Yang, C.T. Williams, J.W. Van Zee, *J. Mater. Eng. Perform.* 17(2008) 785-792.

[5] Y. Chen, K. Hou, C. Lin, C. Bai, N. Pu, M. Ger, *J. Power Sources* 197 (2012)161-167.

[6] C. Lin, C. Chien, J. Tan, Y.J. Chao, J.W. Van Zee, *J. Power Sources* 196 (2011)1955-1966.

[7] Tong Cui, C-W. Lin, C.H. Chien, Y.J. Chao, J. Van Zee. Service Life Prediction of Seal in PEM Fuel Cells[J]. *Proceedings of the SEM Annual Conference*. June 7-10, 2010 Indianapolis, Indiana USA

[8] Tong Cui, Y.J. Chao, J.W. Van Zee. Stress relaxation behavior of EPDM seals in polymer electrolyte membrane fuel cell environment[J]. *international journal of hydrogen energy*, 37 (2012), 13478-13483.

[9] T. Cui, Y.J. Chao, and J. W. Van Zee. Stress Relaxation Behavior of a Liquid Silicone Rubber Seal Subjected to Temperature Cycling[J]. 2011 *The Electrochemical Society*.

[10] Jianning Liu, Panpan Lin, Xiaoxiao Li, Shi-Qing Wang. Nonlinear stress relaxation behavior of ductile polymer glasses from large extension and compression[J]. *Polymer*, 2015, Volume 81, 129-139.

[11] Huimin Li, Boming Zhang, Guanghui Bai. Effects of constructing different unit cells on predicting composite viscoelastic properties[J]. *Composite Structures*. Volume 125, 2015, Pages 459–466.

[12] Jiaohong Zhao, Rui Yang, Rossana Iervolino, Bas van der Vorst, Stellario Barbera. The effect of thermo-oxidation on the continuous stress relaxation behavior of nitrile rubber[J]. *Polymer*

Degradation and Stability. Volume 115, 2015, Pages 32–37.

[13] Vanessa A. Fernandes, Davide S.A. De Focatiis. The role of deformation history on stress relaxation and stress memory of filled rubber[J]. *Polymer Testing*. Volume 40, 2014, Pages 124–132.

[14] T. Rey, G. Chagnon, J.-B. Le Cam, D. Favier. Influence of the temperature on the mechanical behaviour of filled and unfilled silicone rubbers[J]. *Polymer Testing*. Volume 32, Issue 3, 2013, Pages 492–501.

[15] Anja Kömmling, Matthias Jaunich, Dietmar Wolff. Effects of heterogeneous aging in compressed HNBR and EPDM O-ring seals[J]. *Polymer Degradation and Stability*. Volume 126, 2016, Pages 39–46.

[16] Tritala K. Vaidyanathan, Jayalakshmi Vaidyanathan. Validity of predictive models of stress relaxation in selected dental polymers[J]. *Dental Materials*. Volume 31, Issue 7, 2015, Pages 799–806.

[17] Hanna J. Maria, f, Nathalie Lyczko, Ange Nzihou, Kuruvilla Joseph, Cherian Mathew, Sabu Thomas. Stress relaxation behavior of organically modified montmorillonite filled natural rubber/nitrile rubber nanocomposites[J].*Applied Clay Science*. Volume 87, 2014, Pages 120–128.

[18] Ken Yamaguchi, Alan G. Thomas, James J.C. Busfield. Stress relaxation, creep and set recovery of elastomers[J].*International Journal of Non-Linear Mechanics.* Volume 68, 2015, Pages 66–70.