Elastomers and Composites
Vol. 60, No. 1, pp. 11~17 (March 2025)
Print ISSN 2092-9676/Online ISSN 2288-7725
DOI: https://doi.org/10.7473/EC.2025.60.1.11

Study on Interface and Low Temperature Sealing Capability of Thermally Aged CR (Chloroprene Rubber) O-ring

Jin Hyok Lee*, Myung Chan Choi*, Yu Mi Yoon*, Yongsu Jo*, Yongwon Cho*, Sung Han Park, Wonho Kim***, and Jong Woo Bae*,†**

Elastic Material Research Group, Korea Institute of Materials Convergence Technology, Busan 47154, Republic of Korea
***Agency for Defense Development, Yuseong, Daejeon 34186, Republic of Korea*
****Department of Chemical Engineering, Pusan National University, San 30 Jangjeon-dong, Geumjeong-gu, Busan 46241, Republic of Korea*

(Received December 19, 2024, Revised March 26, 2025, Accepted March 31, 2025)

Abstract: In this study, we observed the effect of thermal degradation on the low-temperature sealing capability. A large- sized CR O-ring of 90.0 mm inner diameter and 7.0 mm cross-sectional diameter was used. In FT-IR spectroscopy, the aged CR O-ring, CR-10, showed a carboxyl group upon oxidation. Through oxidation, the sealing force of the aged CR O-rings decreased with an increase in the degree of degradation. As the degree of degradation increased, the 10% compressive modulus had higher values at each relative position. Oxidation was caused by oxygen diffusion to the CR interface. As the degree of degradation increased, glass transition temperature (T_g) was increased, and tan δ was decreased. CR-10 showed -44.0℃ of T_g and 0.89 of tan δ. With an increase in the degree of degradation, the mobility of the CR decreased and showed a slow recovery rate at low temperatures. All specimens showed lower temperature retraction 10 (TR10) than T_g with 2.0-2.5℃ difference. The gas leakage temperature increased with the degree of degradation. This coincided with T_g and TR10 tendency. Under T_g and TR10, CR could still exhibit viscoelastic properties and could be used as a seal. At the gas leakage temperature, the CR changed to a glassy state, and leakage occurred.

Keywords: CR O-ring, Low temperature sealing capability, Temperature retraction (TR), Glass transition temperature (T_g), Modulus profiles

Introduction

Seals include O-rings and gaskets, used to a wide range of industries and became more demanding. The reliability of seals was determined by the ability of the seals to restrict the flow of fluid in the service environment.[1,2] Nowadays, seals are applied to more expensive engineered systems, like nuclear plants, ships, aerospace, etc. The selection process of seals would follow steps; 1) operating temperature, 2) chemical resistance, 3) mechanical properties requirements.[3] In case of the application to expansive engineered system, wide range of operating temperature include extreme low temperature was demanded. While many people researched to operating characteristics and degradation mechanism at high temperature, low temperature sealing capability of seals was less studied. Low temperature sealing capability was usually investigated for developing the new improved seals.

At normal operating temperatures, the molecules in O-rings would be free to rotate, and the individual chain segments would remain flexible. With decreasing temperature, the ability of molecules to rotate would be reduced. At glass transition temperature (T_g), the mobility of molecules and chain segments was minimized. At below glass transition temperature, the O-ring couldn't perform sealing. Degradation of elastomers affected the mobility of the molecules and chain segments. And it induced to low temperature sealing capabilities of O-ring.[4-6]

Elastomers would start the degradation after it was made. Many variables affect the elastomer's degradation, like temperature, light, ionizing radiation, humidity, fluids, etc. In these available, oxygen directly affects elastomer degradation. These effects were significantly interesting on analyzing the degradation mechanism and predicting the life-time. The many techniques used to analyze elastomer

†Corresponding author E-mail: jwbae@kimco.re.kr

degradation and predict the life-time includes modulus profile, oxygen permeability, NMR, TGA, and DTA.[7-9] In previous study, we studied life-time prediction of a CR O-ring using intermittent CSR (Compression stress relaxation) and TTS (Time temperature superposition) principle, and was introduced to previous paper.[10]

In this study, we investigated the thermal degradation effects on low temperature sealing capability. A large sized CR O-ring of 90.0 mm inner diameter and 7.0 mm cross-sectional diameter was used. We prepared aged CR O-rings and specimens by thermal aging test. We analyzed FT-IR and modulus profiles to observe the degradation mechanism. DMA and temperature retraction (TR) tests were used to observe the dynamic and visco-elastic properties. Finally, low temperature sealing capability was tested by low temperature sealing tester.

Experimental

1. Materials

CR O-rings and specimens were supplied from Sam Jung Industrial Co. (South Korea). They had 90.0 mm inner diameter and 7.0 mm cross-sectional diameter. CR S40V (DENKA, Japan) was used as the main matrix of CR O-rings. Table 1 shows the formulation of CR O-rings.

2. Preparation of thermally aged CR O-rings and specimens

In previous study, we analyzed thermal degradation behavior of CR O-ring with intermittent CSR test. Table 2 shows the thermal aging time for preparing thermally aged CR O-rings, which aged to a controlled state of degradation at 120℃. Controlled state of degradation was 70%, 50%, and 10%RSF (Retained sealing force). Thermally aged CR O-rings prepared by aging each scheduled time in 120℃ convection oven. A convection oven, AS-F0-05 model of A-Sung Tester Co. (South Korea), was used for the thermal aging test and preparation of thermally aged CR O-rings which was aged to controlled state of degradation.

Table 1. The Formulation of CR O-ring

Material	CR
DENCA CR S40V	100.0
N 550	45.0
Dibutoxyethoxyethyladipate	5.0
Zinc oxide	5.0
Magnesium oxide	4.0
Stearic acid	0.5
Octylated diphenylamine	1.0
Tri-methylthiourea	1.5
Tetramethyl thiuram monosulphide	0.5
N-cyclohexyl-2-benzothiazole sulfenamid	0.5

3. Measurements

Figure 1 showed how the intermittent CSR test jig was

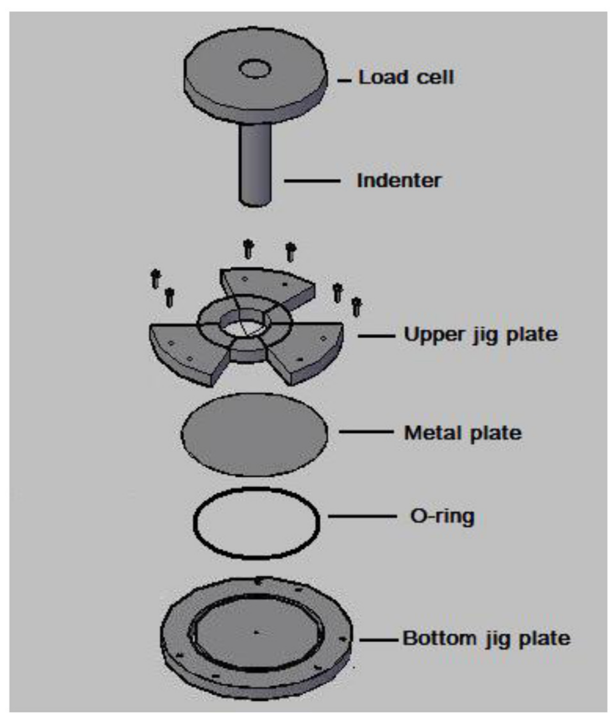

Figure 1. The intermittent CSR test jig.

Table 2. Thermal Aging Time for Preparing Aged CR O-rings and Specimens

Code	CR-I	CR-70	CR-50	CR-30	CR-10
%RSF (%)	100	70	50	30	10
Aging time at 120℃ (hrs)	0	98	196	284	436

designed and manufactured with consideration of how O-rings see service. The groove of the intermittent CSR jig was designed according to KS B 2799(O-ring housing design criteria; Korea Standard). Compression ratio was 15% when CR O-ring was fitted to intermittent CSR test jig. Intermittent CSR tests followed this procedure: 1) CR O-ring was fitted to the jig; 2) the assembled jig was placed to UTM (Universal test machine); 3) Sealing force of CR O-ring was measured by UTM. In intermittent CSR tests an Instron (U.S.A) UTM, 3345(Q3776) model, was used. The indenter was cylindrical of dimensions 25 mm×180 mm (diameter ×height). The test speed was 1.0 mm/min.

Modulus profile was measured as followed steps: 1) Cylinder type specimen (20 mm in diameter and 10 mm in thickness) was used. 2) After the thermal aging test, slice the specimen into five pieces with 2 mm thickness. 3) For each sliced piece, 10% compressive modulus was measured. The test speed was 1.0 mm/min

The JASCO 6100 FT-IR spectrophotometer was used to analysis chemical structure e change of CR O-ring by thermal aging. Resolution was 4 cm^{-1} and 32 scans with ATR mode.

Q800 (TA instruments, U.S.A.) was used to analysis the dynamic mechanical properties with a constant frequency of 1 Hz and the temperature range from -60°C to +80°C. The samples were analyzed by tensile mode with a static load of 1% and dynamic load was 0.5%. The sample size was 60 mm × 12 mm × 2.5 mm.

For observing the visco-elastic properties of each CR, temperature retraction test (TR test) was carried out according to ASTM D1329. EKT-TR100 (Ektron Tek Co., Ltd, U.S.A) was used to TR test at low temperature. TR test was carried out as followed steps. 1) Specimen strained for 50%, 2) cooled down below freezing, 3) measured recovery percentage with increasing temperature.

Lastly, low temperature sealing capabilities were observed by low temperature sealing tester. Figure 2 shows low temperature sealing tester, which was made by us. Low temperature sealing test was progressed by followed procedures: 1) Thermally aged CR O-ring was fitted to groove in sealing test jig (Part 1). 2) Pressurized gas was supplied to line 1. When there was no leak, gas passed to line 2. The gas pressure was 70 bar, and the flow rate was 40 lbs/hr. 3) The temperature of the test jig was continuously decreased. Decreasing velocity of temperature was 2°C/min. Test temperature could be controlled to -60°C. 4) When gas leak occurred, it was detected and recorded by the mass flow meter.

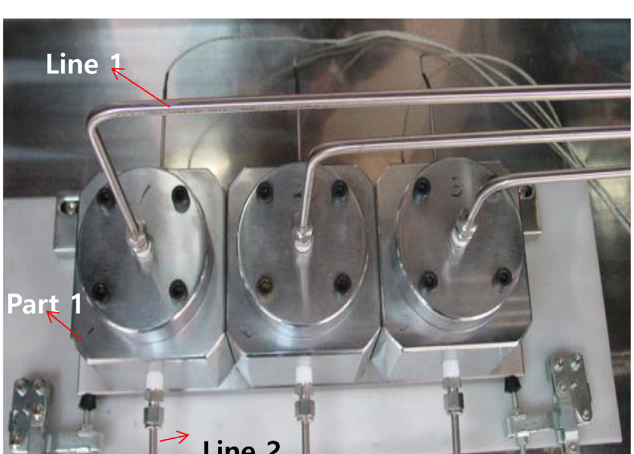

Figure 2. Low temperature sealing tester.

Results and Discussion

1. Degradation of CR O-rings

Sealing force of thermally aged CR O-rings was measured by intermittent SCR test. Figure 3 shows the measured sealing force and %RSF. With increasing thermal aging degradation, sealing force was decreased. In Table 3, we arranged the relationship between aging time, sealing force and %RSF of CR O-rings. Each CR O-ring showed suitable sealing force to control the state of degradation under ±1% deviation. We confirmed and successfully prepared thermally aged CR O-rings

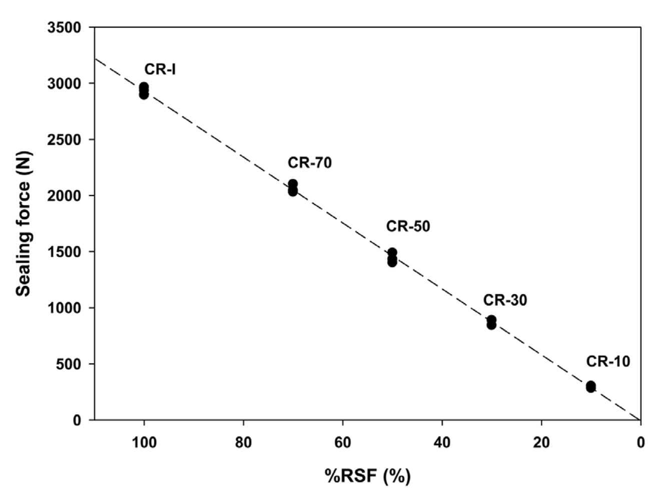

Figure 3. Sealing force of CR O-rings according to %RSF after thermal aging test.

Table 3. Sealing Force of CR O-rings According to %RSF after Thermal Aging Test

	CR-I	CR-70	CR-50	CR-30	CR-10
%RSF (%)	100	70	50	30	10
Sealing force (N)	2931	2058	1441	873	295
Real %RSF (%)	100	70.2	49.1	29.8	10.1
Deviation (%)	0	+0.2	-0.9	-0.2	+0.1

2. FT-IR spectroscopy

Figure 4 showed FT-IR analysis result. From IR spectrum of CR-I, unaged CR O-ring showed some of characteristic features expected for CR. Spectrum of CR-I shows C-Cl stretching and bending band at 825 cm^{-1}, -CH_2 band at 1450 cm^{-1}, C=C band at 1660 cm^{-1}, CH_2 symmetric band at 2848 cm^{-1}, CH_2 asymmetric band at 2917 cm^{-1}, and OH band at 3450 cm^{-1}. In the spectrum of CR-10, hydroxyl (3450 cm^{-1}) was broadly increased, and conjugated carbonyl (1660 cm^{-1}) was increased.[11] It was caused by oxidation of CR. In thermal aging, oxygen diffused to CR inside, and oxidation reaction occurred in CR backbone. Caused by this oxidation, sealing force was decreased with increasing thermal aging time.

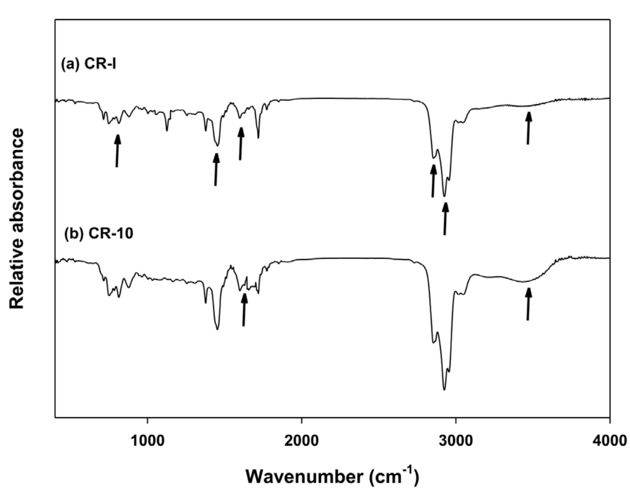

Figure 4. FT-IR spectra; (a) CR-I, and (b) CR-10.

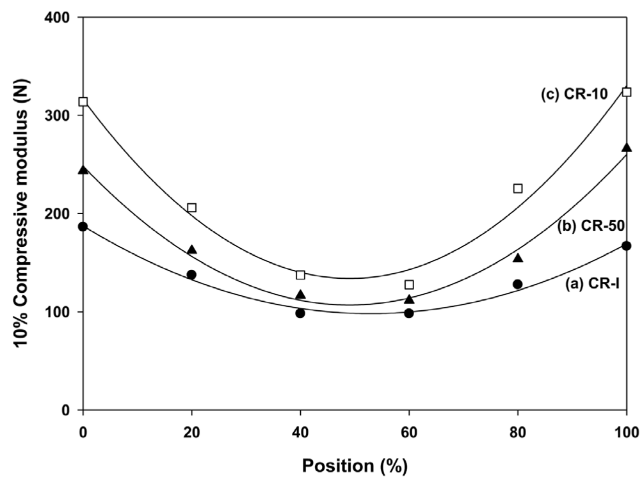

Figure 5. Modulus profile for 2 mm thickness CR specimens after thermal aging test; (a) CR-I, (b) CR-50, and (c) CR-10.

3. Modulus profile

For observing the interface change by degradation, we measured the modulus profile of CR-I, CR-50, and CR-10, as shown in Figure 5. The outside of the specimen, 0% and 100% positions showed the highest 10% compressive modulus. Whereas the inside of the specimen, 40~60% position showed the lowest 10% compressive modulus.[12] Because of degradation of the CR was dependent on oxygen diffusion. Therefore, the level of oxygen diffusion differed according to the position, and the specimen surface showed a faster degradation rate than the center of the specimen. CR-I showed an 88 N deviation in modulus according to the position, but CR-10 showed a 196 N deviation. At the 40% and 60% positions, CR-I showed a 10% lower compressive modulus than CR-10 because CR-I had a lower degree of degradation than CR-10.

4. DMA analysis

We analyzed DMA and results were shown in Figure 6. All the samples showed different T_g and tanδ. With increasing the degree of degradation, T_g was increased, and tan δ was decreased. By thermal degradation, oxidation occurred to the CR backbone. With increasing the degree of degradation by oxidation, mobility was decreased, and stiffness was increased.[13] These influenced to change of tanδ and T_g.

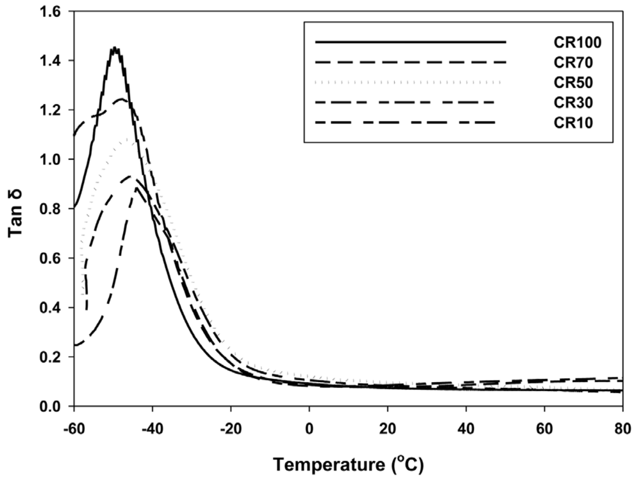

Figure 6. Dynamic loss tangent of CR specimens according to the degree of degradation.

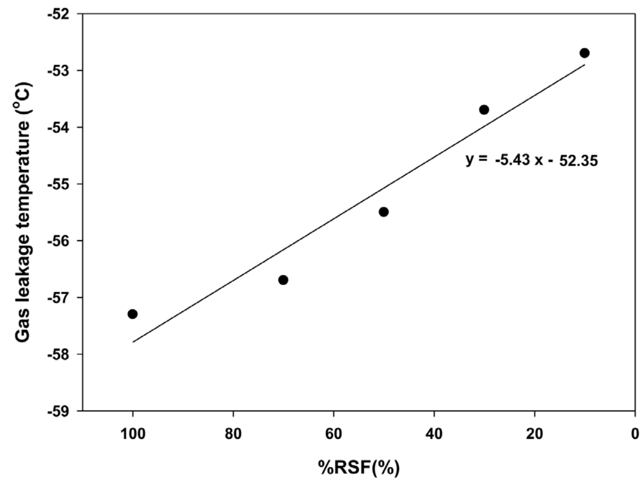

Figure 8. Gas leakage temperature of CR O-rings according to %RSF.

CR-I showed 49.7°C of T_g and 1.45 of tan δ. CR-10 showed -44.0°C of T_g and 0.89 of tan δ. Compared with CR-I, T_g of CR-10 was increased about 5.7°C of T_g and decreased 38.6% of tan δ.

5. TR test

The visco-elastic property was observed by the TR test, and the results are shown in Figure 7. TR10 of CR-I was -52.16°C, 2.4°C lower than T_g. TR10 increased with the degree of degradation. With increasing the degree of degradation, the mobility of CR decreased and showed a slow recovery rate at low temperatures. All specimens showed lower TR10 than T_g with 2.0~2.5°C difference. We confirmed that CR could still have mobility under T_g. Also, the TR70-TR10 values of all specimens were approximately 7.5°C. It seems that the degree of degradation affected mobility, but the recovery rate would be similar at low temperatures.

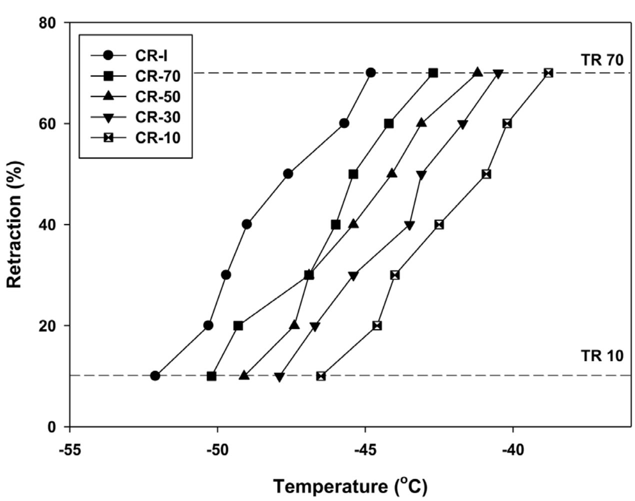

Figure 7. Temperature retraction curves of CR specimens according to %RSF.

6. Low temperature sealing capability

Sealing capability of CR O-rings was tested by low temperature sealing tester, and the results were shown in Figure 8. Gas leakage temperature increased with increasing the degree of degradation. It coincided with T_g and TR10 tendency. Mobility of CR directly affected to low temperature sealing capability. Gas leakage temperature was lower than TR10 about 5.2~6.4°C, and lower than T_g about 7.6~9.0°C. Under T_g and TR10, CR could still have

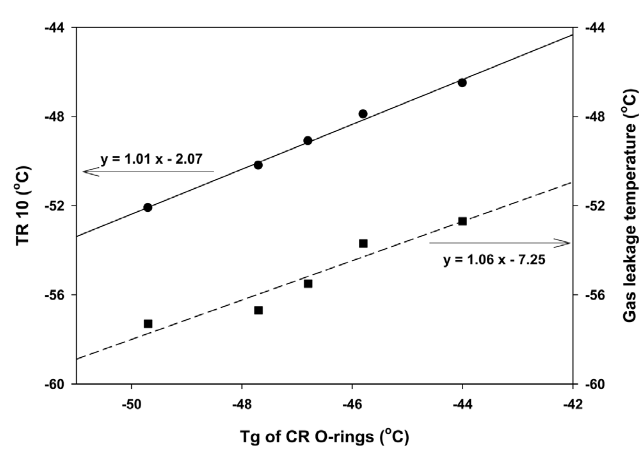

Figure 9. Change of TR10 and gas leakage temperature according to T_g of thermally aged CR.

visco-elastic property and performed as the seal. At the gas leakage temperature, CR changed to a glassy state, and a leak occurred. Gas leakage temperature and %RSF showed the following relationship: y=-5.43x-52.35.

According to T_g changing, the relationship with TR10 and gas leakage temperature is depicted in Figure 9. With the increase of the degree of degradation, mobility decreased but could still be maintained at a lower temperature than T_g. T_g and TR10 showed the following relationship: y = 1.01x-2.07. Also, T_g and gas leakage showed the following relationship: y=1.06x-7.25.

Conclusions

In this study, we observed the thermal degradation effect on low temperature sealing capability. We successfully prepared CR O-rings and specimens with controlled degree of degradation. In FT-IR spectroscopy, aged CR O-ring; CR-10, showed carboxyl group by oxidation. By oxidation of the CR backbone, the sealing force of aged CR O-rings decreased with increasing the degree of degradation. With increasing the degree of degradation, 10% compressive modulus had higher values at each relative position. It was caused by oxidation caused by oxygen diffusion, and the modulus of the inside position increased with the degree of degradation. As the degradation degree increased, T_g was increased while tan δ decreased. Because of oxidation degradation, mobility decreased, and stiffness increased. CR-10 showed -44.0°C of T_g and 0.89 of tan δ. With increasing the degree of degradation, the mobility of CR decreased and showed a slow recovery rate at low temperatures. All specimens showed lower TR10 than T_g with 2.0~2.5°C difference. Gas leakage temperature increases with the degree of degradation. It coincided with T_g and TR10 tendency. Gas leakage temperature was lower than TR10, about 5.2~6.4°C, and lower than T_g, about 7.6~9.0°C. Under T_g and TR10, CR could still have visco-elastic properties and perform as the seal. At the gas leakage temperature, CR changed to a glass state, and a leak occurred.

Acknowledgements

This research was supported by The Development of -70°C Cryogenic, Hydrogen-resistant Elastomer for 70 MPa Hydrogen Tanks in Commercial Vehicles (RS-2024-00439388) project, the Development of Highly Corrosion-Resistant Elastomers and Application Technologies for Ammonia-Fueled Marine Propulsion Systems with a Voluem Change Rate of Less than 10% (RS-2024-00439861) and the Development of Large-Area Multilayer High-Damping Insulation Pads with 30 mW/mK Grade Using Supercritical Foaming Technology (RS-2024-00433288) project, all supported by the Ministry of Trade, Industry and Energy.

Conflict of Interest: The authors declare that there is no conflict of interest.

References

1. P. Warren, A. Douglas, and P. Embury, "Low temperature sealing capability of O-rings: the relationship between laboratory tests and service performance", In *Conference on High Performance and Speciality Elastomers, RAPRA* (2007).
2. B. Flitney, "How should we rate the temperature capabilities of elastomers", *Sealing Technology,* **2007**, 6 (2007).
3. P. Warren, "Low temperature sealing capability of elastomer O-rings", *Sealing Technology,* **2008**, 7 (2008).
4. P. Farrow and F. Merli, "New low temperature perfluoroelastomer for effective sealing within the chemical process industries", *'20th International Conference on Fluid Sealing, BHR Group*, 189 (2009).
5. D. R. Bronowski, "Performance testing of elastomeric seal materials under low and high temperature conditions", *Sandia National Laboratories,* (2000).
6. G. Gee, "The thermodynamic analysis of the effect of pressure on the glass temperature of polystyrene", *Polymers*, **7**, 177 (1966).
7. M. Cellina, K. T. Gillen, and R. A. Assink, "Accelerated aging and lifetime predictions: Review of non-Arrhenius behavior due to two competing processes", *Polymer Degradation and Stability*, **90**, 395 (2005).
8. K. T. Gillen, J. Wise, and R. L. Clough, "General solution for the basic autoxidation scheme", *Polymer Degradation and Stability,* **47**, 149 (1995).
9. K. T. Gillen and R. L. Clough, "Oxygen diffusion effects in thermally aged elastomers", *Polymer Degradation and Stability,* **38**, 47 (1992).
10. J. H. Lee, J. W. Bae, J. S. Kim, T. J. Hwang, S. D. Park, S. H. Park, T. M. Yeo, W. Kim, and N. J. Jo, "Life-time prediction of a chloroprene rubber (CR) O-ring using intermittent compression stress relaxation (CSR) and time-temperature superposition (TTS) Principle", *Macromolecular Research,* **19**, 555 (2011).

11. M. Celina, J. Wise, K. K. Ottesen, K. T. Gillen, and R. L. Clough, "Correlation of chemical and mechanical property changes during oxidative degradation of neoprene", *Polymer Degradation and Stability,* **68**, 171 (2000).
12. P. Y. Le Gac, V. Le Saux, M. Paris, and Y. Marco, "Ageing mechanism and mechanical degradation behaviour of polychloroprene rubber in a marine environment: Comparison of accelerated ageing and long term exposure", *Polymer Degradation and Stability.* **97**, 288 (2012).
13. A. Das, F. R. Costa, U. Wagenknecht, and G. Heinrich, "Nanocomposites based on chloroprene rubber: Effect of chemical nature and organic modification of nanoclay on the vulcanizate properties", *European Polymer Journal,* **44**, 3456 (2008).