Application News

DSC-60 Plus Differential Scanning Calorimeter
DTG-60 Simultaneous Thermogravimetric and Differential Thermal Analyzer
TMA-60 Thermomechanical Analyzer

# Evaluation of Thermal Characteristics of Rubber O-Rings

Atsushi Kawaguchi

## User Benefits

- The DSC-60 Plus enables measurements down to temperatures as low as -140 °C by filling the standard built-in cooling bath with liquid nitrogen.
- The DTG-60 supports simultaneously evaluation of the heat resistance of rubber samples and quantitative analysis of the sample components.
- The TMA-60 enables stable measurement of the coefficient of linear expansion, even under a small compressive load of 10 mN.

## ■ Introduction

High sealability is required in piping and vessels used in the transportation and storage of gases and liquids in order to prevent leaks. In particular, because leaks occur easily at joints, rubber seal materials such as O-rings are frequently used to improve the sealability of these parts. Since the characteristics of rubber, including the applicable temperature range, pressure resistance, and weathering resistance, differ depending on the type of material, it is necessary to select a suitable seal material for the intended purpose and use environment. This article introduces an example of a total evaluation of the thermal characteristics of four types of rubber O-rings made from different materials, which were measured using a Shimadzu Differential Scanning Calorimeter (DSC), Simultaneous Thermogravimetric and Differential Thermal Analyzer (TG-DTA), and Thermomechanical Analyzer (TMA).

## ■ Analysis Samples

Four types of rubber O-rings made from different materials were measured using each of the instruments. Table 1 shows the materials of each O-ring.

Table 1 List of Analysis Samples

| | |
|---|---|
| • Ethylene propylene rubber (EPDM) | • Fluororubber (FKM) |
| • Nitrile rubber (NBR) | • Silicone rubber |

## ■ Evaluation of Cold Resistance by DSC

Rubber generally loses its elasticity when the temperature drops to the glass transition point. If the seal material loses its elasticity, its sealability decreases and there is a danger of leakage. Thus, it is important to confirm the glass transition point in order to set the applicable temperature range in the low temperature region and ensure safety. The glass transition point can be measured by DSC. Here, the EPDM, NBR, and FKM samples were measured using a DSC-60 Plus, which enables refrigerated measurement to temperatures as low as -140 °C by filling the standard cooling bath with liquid nitrogen. Since the cooling bath is incorporated in the instrument itself, measurement is possible even without an optional cooling device. In this measurement, liquid nitrogen was introduced, and the measurement was started after reaching the measurement starting temperature of -70 °C. Table 2 shows the measurement conditions of the EPDM, NBR, and FKM, and Fig. 1 shows the measurement results.

Table 2 DSC Measurement Conditions of EPDM, NBR, and FKM

| | |
|---|---|
| Instrument | : DSC-60 Plus |
| Cell | : Aluminum crimp cell |
| Heating rate | : 10 °C/min |
| Temperature pattern | : -70 °C → 100 °C |
| Atmosphere | : Nitrogen, 50 ml/min |

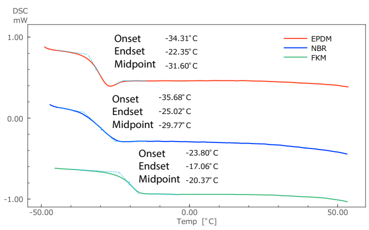


Fig. 1 DSC Measurement Results of EPDM, NBR, and FKM

From Fig. 1, the onset temperatures of the glass transition point were -34.3 °C for EPDM, -35.7 °C for NBR, and -23.8 °C for FKM.

Next, the silicone rubber sample was measured. Unlike EPDM, NBR, and FKM, silicone rubber undergoes crystallization and loses its elasticity due to hardening at low temperatures. Therefore, the crystallization temperature was determined by a temperature-fall measurement from room temperature. Table 3 and Fig. 2 show the measurement conditions and measurement results, respectively.

Table 3 DSC Measurement Conditions of Silicone Rubber

| | |
|---|---|
| Instrument | : DSC-60 Plus |
| Cell | : Aluminum crimp cell |
| Cooling rate | : 5 °C/min |
| Temperature pattern | : Room temperature → -100 °C |
| Atmosphere | : Nitrogen, 50 ml/min |

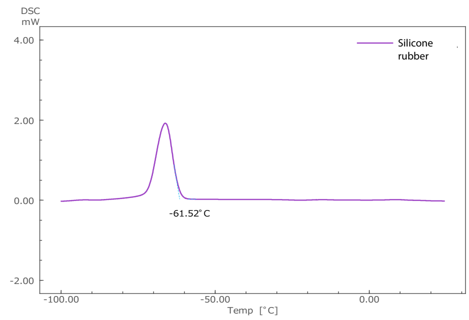


Fig. 2 DSC Measurement Results of Silicone Rubber

From Fig. 2, it was found that the silicone rubber sample crystallizes at -61.5 °C. The results shown in Fig. 1 and Fig. 2 suggested the possibility that silicone rubber maintains its elasticity to the lowest temperature among these samples.

## ■ Evaluation of Heat Resistance and Quantitative Analysis of Components by TG-DTA

When the temperature is raised, rubber decomposes upon reaching the decomposition temperature. Since the decomposition temperature is used as an indicator of heat resistance, confirmation of this property is important from the viewpoint of setting the applicable temperature range and ensuring safety. In addition, carbon black or various types of inorganic materials are generally added to rubber as reinforcing agents. It is also important to confirm the blending ratio in the manufacturing process because the properties of the rubber change when the blending ratio of the various components is altered. In measurements of rubber by TG-DTA, simultaneous measurement of the decomposition temperature of the rubber and quantitative analysis of its various components is possible. Here, the measurements were carried out using the DTG-60. Table 4 shows the measurement conditions, Fig. 3 shows the TG measurement results for each sample, and Table 5 shows the values of 1 % decrease (weight loss) temperature, the decrease ratio, and the percentage of residue of each sample calculated from the TG measurement results.

Table 4 TG-DTA Measurement Conditions

| | |
|---|---|
| Instrument | : DTG-60 |
| Cell | : Platinum cell |
| Heating and cooling rate | : 20 ˚C/min |
| Temperature pattern and atmosphere | : Room temperature → 300 ˚C → 550 ˚C → 650 ˚C → 300 ˚C<br>Nitrogen, 300 ml/min<br>300 ˚C → 650 ˚C<br>Air, 300 ml/min |

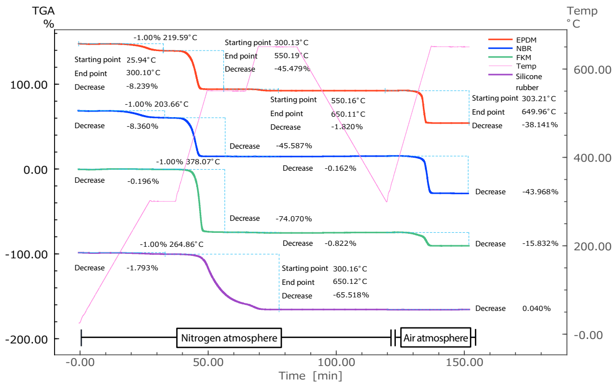


Fig. 3 TG Measurement Results

Table 5 Values of 1 % Weight Loss Temperature, Decrease Ratio, and Residue of Samples

| | 1 % weight loss temperature (˚C) | Decrease ratio (%) | | | | Residue (%) |
|---|---|---|---|---|---|---|
| | | Nitrogen atmosphere | | | Air atmosphere | |
| | | Room temp. to 300 ˚C | 300 ˚C to 550 ˚C | 550 ˚C to 650 ˚C | 300 ˚C to 650 ˚C | |
| EPDM | 219.6 | 8.2 | 45.5 | 1.8 | 38.1 | 6.4 |
| NBR | 203.7 | 8.4 | 45.6 | 0.2 | 44.0 | 1.8 |
| FKM | 378.1 | 0.2 | 74.1 | 0.8 | 15.8 | 9.1 |
| Silicone rubber | 264.9 | 1.8 | 65.5* | | 0.0 | 32.7 |

* With the silicone rubber, because decrease (weight loss) during heating from 300 ˚C in the nitrogen atmosphere was not completed at the holding temperature of 550 ˚C, the decrease is read in the range from 300 ˚C to 650 ˚C.

In this measurement, the 1 % weight loss temperature was defined as the decomposition start temperature. From Table 5, NBR displayed the lowest 1 % weight loss temperature, while FKM showed the highest value. Based on these results, it was suggested that FKM has the highest heat resistance among the samples used in this measurement.

Focusing on the decrease ratios of EPDM, NBR, and FKM, the decrease in the temperature range from room temperature to 300 ˚C in the nitrogen atmosphere is considered to be due to the thermal decomposition of organic substances other than rubber. Since almost no decrease was observed in FKM in this temperature range, it can be understood that FKM does not contain organic substances other than rubber. The decrease in the temperature range from 300 ˚C to 550 ˚C is considered to be due to the thermal decomposition of organic components that were not volatilized at 300 ˚C and the main component of rubber. The total of the decrease from room temperature to 300 ˚C and the decrease from 300 ˚C to 550 ˚C shows the total amount of organic components, and indicates that FKM has the largest organic content. The decrease from 550 ˚C to 650 ˚C is attributed to decomposition of partial inorganic fillers.

The decrease in the temperature range from 300 ˚C to 650 ˚C after switching to an air atmosphere is thought to be the result of oxidative decomposition of carbon black, which is added to rubber as a reinforcing agent. This measurement showed that NBR has the highest content of carbon black.

Next, focusing on silicone rubber, the decrease (weight loss) during heating from 300 ˚C in the nitrogen atmosphere was not completed at the holding temperature of 550 ˚C, and continued to occur until 650 ˚C. For this reason, it is not possible to quantify the organic components that were not volatilized at 300 ˚C, the main component of rubber, and the partial inorganic filler. However, since no weight loss occurred under heating from 300 ˚C to 650 ˚C in the air atmosphere, it can be concluded that this silicone rubber sample does not contain carbon black. Finally, a residue remained at the end of measurement of all the rubbers. This residue is ash, which is not decomposed even under heating up to 650 ˚C in an air atmosphere. Thus, a quantitative analysis of the components in the rubber samples can be conducted simultaneously with evaluation of the heat resistance of the various types of rubber by this type of TG-DTA measurement.

## ■ Measurement of Coefficient of Linear Expansion by TMA

O-rings are used under a condition in which the O-ring is fitted in a groove and crushed appropriately. Since there is a danger of reduced sealability, damage, or deterioration if large thermal expansion or thermal contraction occurs, it is important to take the coefficient of expansion into account in the design. The coefficient of linear expansion can be measured by using TMA. Here, the coefficients of linear expansion of each sample were measured by using the TMA-60. Table 6 and Fig. 4 show the measurement conditions and measurement results, respectively.

Table 6 TMA Measurement Conditions

| | |
|---|---|
| Instrument | : TMA-60 |
| Measurement mode | : Expansion mode |
| Heating rate | : 5 ˚C/min |
| Temperature pattern | : -30 ˚C → 50 ˚C |
| Compressive load | : 10 mN |
| Atmosphere | : Nitrogen, 50 ml/min |

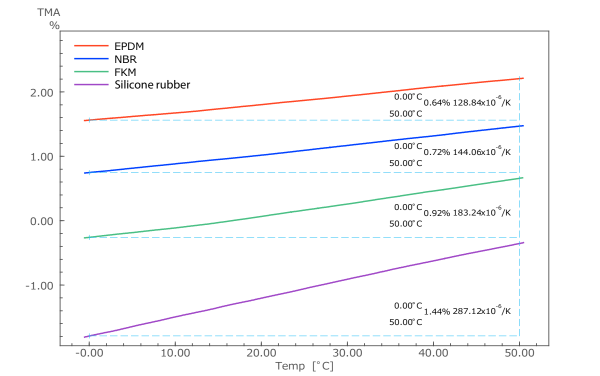


Fig. 4 TMA Measurement Results

Although these measurements were carried out under a small compressive load of 10 mN, all the samples displayed linear expansion, demonstrating that stable measurement is possible even under a low load. The coefficients of linear expansion obtained in the temperature range from 0 ˚C to 50 ˚C decreased in the order of silicone rubber > FKM > NBR > EPDM, showing the EPDM has the smallest thermal expansion in the temperature range among the samples used in this measurement.

## ■ Conclusion

An evaluation of cold resistance by DSC, evaluation of heat resistance and quantitative analysis of sample components by TG-DTA, and measurement of the coefficient of linear expansion by TMA were carried out for four types of rubber O-rings. Since clear differences between the respective samples were confirmed, these thermal analysis instruments are considered to be effective tools for evaluation of the thermal characteristics of rubber.

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